

THE TANNINS

HENRY TRIMBLE

— CN June 1-94

The Tannins : a Monograph of the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents. With an Index to the Literature of the Subject. By HENRY TRIMBLE, Ph.M., Professor of Analytical Chemistry in the Philadelphia College of Pharmacy. Volume II. The Tannins of Oak-bark, Mangrove, Canaigre, Chestnut. London and Philadelphia : Lippincott Co. 1894.

THE author tells us in his preface that he has examined the astringent principles of nine species of oaks, and one species each of mangrove, canaigre, and chestnut. In the former volume he discussed the tannins as a class, and the pathological tannins of gall-nuts.

The tannins of catechu, myrobalans, sumac, the wattle-barks, &c., do not receive an extended notice. This is the more to be regretted since these substances, if less interesting to the tanner, are more important to the dyer. Oak-barks, mangrove, and canaigre concern the colour chemist but little. The same may be said of the chestnuts, which furnish a tannin sometimes encountered where it is unwelcome, *i.e.*, in the sophistication of extracts of logwood.

The oak-barks are certainly here dealt with in a very thorough manner. Their reactions, their localities, their botanical identification are all carefully and elaborately expounded.

For the analysis of the oak-barks the author gives the preference to "the practical, but rather unscientific hide-powder method."

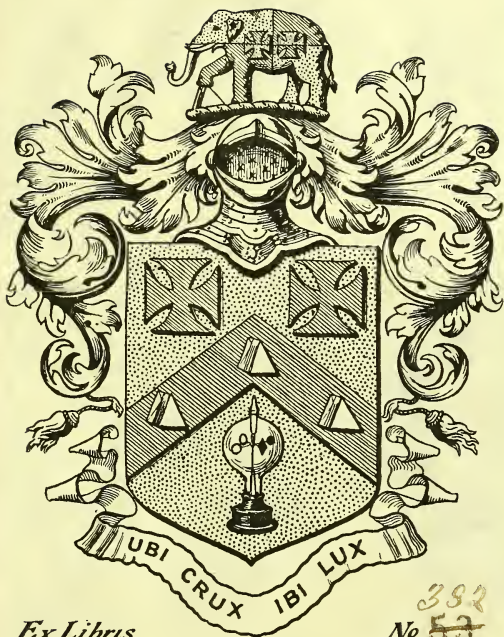
Chestnut-wood is admittedly poor in tannin, Mr. Trimble finds in the air-dried chips 7.85 per cent. and in the bark only 7.31.

The ultimate composition of the tannins is far from identical in the gallotannic acid and in the tannins of chestnut-wood and bark, and in that of sumac the carbon is 52 per cent. In pomegranate-bark it is 50. In the tannins of oak-bark, mangrove, canaigre, rhatany, kino, catechu, and tormentil it ranges, according to various chemists, from 58.10 to 59.79.

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THE TANNINS.

A MONOGRAPH ON THE HISTORY, PREPARATION
PROPERTIES, METHODS OF ESTIMATION,
AND USES OF THE VEGETABLE
ASTRINGENTS,

WITH AN INDEX TO THE LITERATURE OF THE
SUBJECT.

BY

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OF PHARMACY.

VOLUME II.

THE TANNINS OF

OAK BARK,
MANGROVE,

CANAIGRE,
CHESTNUT.

PHILADELPHIA:

J. B. LIPPINCOTT COMPANY.

1894.

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P R E F A C E.

THIS second volume of *The Tannins* is devoted to the results of investigation by the author on the astringent principles from nine species of oaks and one species each of mangrove, canaigre, and chestnut.

In accordance with the announcement made in Volume I., there has been associated with these results so much descriptive matter, from the author's observations and other sources, as has been necessary to complete a foundation for the intelligent study of the subject.

The sources of these tannins have received careful attention, and every precaution taken to insure the genuineness of the samples from which the tannin was extracted.

The various oak barks were collected by the author himself or his assistant, with the exception of two samples, one from Dehra Dún, India, the other from Herefordshire, England. The two last-mentioned specimens were obtained in anticipation of a possible criticism, that only the tannins from the oaks of North-eastern United States were investigated. Having employed material from three different quarters of the globe, it is reasonable to assume that the conclusions regarding the oak tannins are not based on too narrow foundations.

Since the issue of the first volume the gathering of the bibliography has been steadily carried on. Many sources, not then accessible, have been consulted, so that now, in the two volumes, this index contains a total of nearly one thousand titles.

The illustrations are from pen drawings by my friend Edwin Thorpe, who possesses that rare combination of artistic and botanical knowledge which eminently fits him for the work ; to him are due my sincere thanks for the special consideration which he gave to this subject for the present volume.

Much credit is due to my assistant J. C. Peacock for his untiring energy and devotion to the chemical investigations. The constant attention necessary to conduct these could not have been given by the author alone, and it is not too much to say that without his assistant's help this volume could not have been written when it was.

My thanks are also due to Professor H. R. Procter, of Leeds, England, for the sample of Herefordshire oak bark and for contributions to the bibliography, and to David Hooper and A. E. Wild, both located in India, for samples of oak bark from the Himalayas.

It may not be out of place here to make it known that the author is very desirous of samples of bark from *Quercus infectoria*, in Asia Minor ; also that he would like specimens of bark from the most important oaks of our Pacific slope. In all cases the botanical origin should be known absolutely beyond a doubt.

H. T.

PHILADELPHIA, April 2, 1894.

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INTRODUCTION.

THE first volume of this work was confined to a discussion of the tannins as a class and the one tannin from nutgalls which may be said to stand by itself.

The present volume will consider a few of what are known as physiological tannins. None of these have been studied with anything like the exactness which has characterized the investigations of gallotannic acid.

Some of them are, no doubt, identical with the tannin from nutgalls, but the great majority appear to be differently constituted.

The tannins have been studied from various directions. Many investigators have approached them from the stand-point of the analytical chemist, others from a botanical direction, and a few with a view of determining their constitution, and other purely chemical relations; the latter naturally include their composition and behavior towards chemical reagents.

The first question that always suggests itself in the study of this class of compounds is a physiological one, which the botanist strives to answer, but he finds that before he can make any real progress he must be able to accurately *estimate* the various tannins; so, in endeavoring to answer this physiological problem, we are confronted by the analytical one. The analytical chemist cannot accomplish satisfactory progress until

he has a definite compound upon which to work. We find, therefore, that first we must know how to obtain a tannin from its source, not necessarily quantitatively, then we must learn to know its physical and chemical properties, and finally its composition and constitution. Having accomplished this much, we are in a position to devise a method of quantitatively determining it. With our chemical knowledge of a tannin and a method of accurately estimating it, we would be prepared to undertake its physiological relations.

After some attempts in each of the above-mentioned departments, the author has decided that the only logical method of pursuing this study is to take up the individual tannins in the following order :¹

(1) The source from which each may be obtained.

(2) Collect what has been accomplished by others ; that is, study the history.

(3) Devise a method of preparation adapted to the peculiar tannin under consideration.

(4) Determine as far as possible its purity, then its physical and chemical properties, composition, and constitution.

(5) Construct an accurate and rapid method of estimation.

Each tannin will then be ready for the plant physiologist.

In the short space of a lifetime it is not possible for one person to accomplish all the research necessary for him to speak with the authority of personal experience

¹ In a few instances the order of (1) and (2) is reversed, and the history given first.

concerning each of the various tannins, or even of a very few of them. This volume, therefore, will be continued in the lines laid down in its predecessor; that is, state what has already been done by others, and combine it with as much original investigation as the author has been able to give to the subject. It is thought this may thereby form a foundation on which others may build, and on which he may continue the work.

One of the most interesting departments in this study is that which considers the physiological questions of the origin and function of the tannins in the vegetable kingdom. It is probably not far wrong to acknowledge that little is known of the functions of any plant constituent, so that in saying, nothing is known of the use of the tannins in the vegetable economy, we are only admitting what is true of all other plant constituents, be they crystalline or amorphous.

There has been much discussion in recent years concerning the function of calcium oxalate, a compound about whose composition and constitution there can be no doubt. If, therefore, this be true of such a well-known substance, it is still more the fact of the tannins, whose constitution is a matter of conjecture.

No final classification of the tannins can be attempted until more of them have been studied. The order in which they will be considered will, therefore, depend quite as much on the supply of material for their preparation as on any other consideration. Eventually their classification must be a chemical one, and until more is known of their composition this cannot be completed.

THE TANNINS.

SECTION I.

SOURCES OF THE OAK TANNINS.

THE sources of the oak tannins, so far as we know at present, are the bark and wood of the oak.

It is not known that all the different species of oaks yield the same tannin. Böttiger has claimed that the tannins from the wood and bark are different. It is certain that the galls of *Quercus infectoria* yield a different tannin from that of the bark and wood of some other species of oaks, and it is reasonable to suppose that the tannin from the galls is identical with that from the bark on which the galls are produced, therefore we may look for a variation in the properties and composition of the tannins from different species.

The supply of oak tannin is obtained from the bark of various oak species. The tannin is not prepared on a commercial scale or used in a pure condition, but either as a weak infusion or as an extract. A considerable quantity of extract prepared from oak wood is found in commerce.

Of the European oaks that are employed for tanning or preparing extract, only a few are worthy of especial

mention, namely, *Quercus robur*, L., and its varieties *sessiliflora*, Sm., known in Germany as *Traubeneiche* or *Wintereiche*, and *pedunculata*, Ehrh., the German *Stieleiche* or *Sommereiche*. The *Quercus sessiliflora* grows chiefly in the mountainous districts and the *Q. pedunculata* on the plains. A leaf of *Q. robur* one-half natural size is shown in Fig. 1, and the acorn natural size in Fig. 2.¹ *Quercus Cerris*, L., *Zerreiche*, grows in Southern and Southeastern Europe, and *Q. pubescens*, Willd., in the more westerly sections. The American Red Oak, *Q. rubra*, L., has been cultivated in some districts on the Rhine, with satisfactory results. The *Q. Cerris* and *pubescens* are the most extensively employed in Austria and Hungary. Slavonia is, perhaps, the chief oak-producing district of Europe. The two varieties of *Q. robur* merge into each other to such an extent that it is difficult to distinguish them in every case.

The *Quercus Suber*, L., or Cork Oak of Southern Europe, is somewhat used, and considerable quantities are sent to Ireland. In the south of France, Spain, and Portugal the Kermes Oak, or *Q. coccifera*, L., is considerably employed. In Southern France, Spain, and Italy the *Quercus Ilex*, L., or Evergreen Oak, is extensively grown, and the bark used not only in that locality, but in various other parts of Europe. The two last-mentioned species are also extensively distributed in Algeria and the other districts surrounding the Mediterranean. There are a large number of oak spe-

¹ In the following illustrations the acorns are natural size, while the leaves are one-half natural size unless otherwise stated in the text.

cies distributed through Europe, whose use is confined to the locality in which they are grown.

In Europe the oaks are barked while still smooth,

FIG. 1.

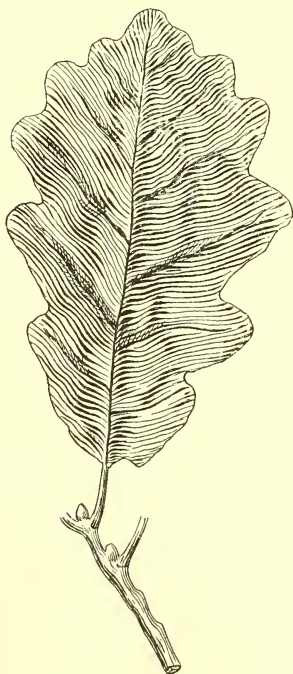
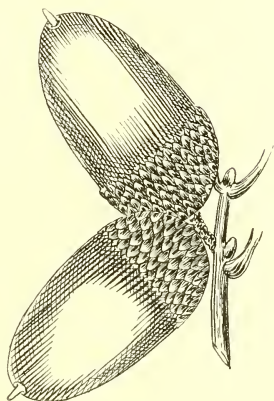


FIG. 2.



Quercus robur, L.
ENGLISH OAK.

that is, before there is any formation of corky layer. This bark is known in Germany as *Spiegelrinde*. The bark collected with a thick corky layer is in very little demand. Many of the oak species do not retain

a smooth bark after they have reached the age of fifteen years, although the *Q. Cerris* is said to be free from cork until it has attained the age of twenty-five years. The rapid destruction of the forests has resulted in the systematic cultivation of the oak, notably in France, Germany, and to a lesser extent in Austria. Some of the forests in Westphalia have been cultivated since the fifteenth century, but this has been scientifically conducted in the other parts of Germany only since 1840.

The collection of bark is usually made from trees fourteen to twenty years old, although sometimes they are allowed to reach the age of thirty-five years before barking.

On account of the readiness with which the bark is removed in May and June the harvest is conducted in those months. It has frequently been suggested to gather the bark in winter when labor is cheaper. As the bark does not strip off easily at that season, various devices have been offered for remedying this difficulty, one of which is to steam the bark thoroughly, which causes it to easily separate.

When the bark is collected from older trees, the corky layer is first removed, while the bark is still on the tree. The process of removing the outer layer in this country is called "rossing."

In some cases the trees are barked while standing, but oftener they are first cut down, and then the bark is readily removed from the whole length of the trunk.

It is considered that the climate affects the yield of tannin considerably. The more southerly and warmer climate is preferred, and especially the southern exposure of mountains. There has been great diversity

of results among investigators concerning the yield of tannin in barks collected at different seasons of the year, but it is generally concluded that the barks gathered in May and June are the richest in astringent principle.

For a more detailed account of the European oaks the reader is referred to "Die Gerbrinde," by J. G. Neubrand, 1869; "Die Rohstoffe des Pflanzenreiches," by Dr. Julius Wiesner, 1873; "Die Gerberinden," by Dr. Franz R. v. Höhnelt, 1880; "Répartition du Tannin dans les diverses régions du bois de Chêne," by E. Henry, 1888.

In North America the available species of oaks are much more numerous than in Europe, and the question of which one shall be used is often solved by its proximity to the tannery or the extract works.

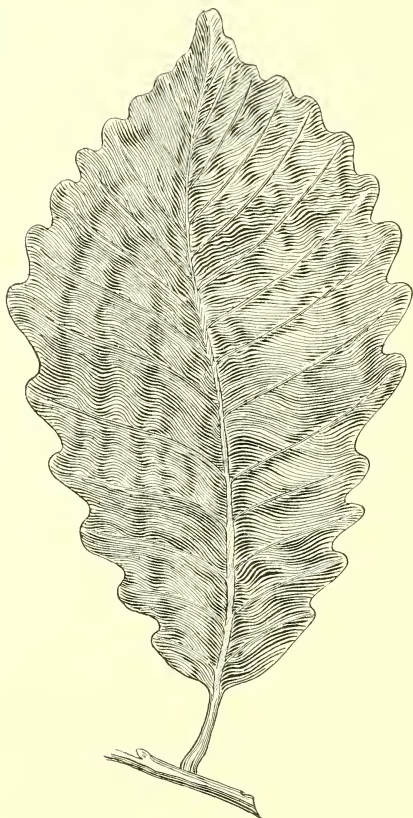
The most popular species for tanning purposes is the *Quercus Prinus*, L., Chestnut Oak, or Rock Chestnut Oak. This includes the variety *monticolor* of Michaux.

The Chestnut Oak is distributed in Eastern United States from Massachusetts to Delaware, and along the mountains as far south as Alabama. It is especially abundant in the mountains of Pennsylvania, and may be found within fifteen miles of Philadelphia on the hills skirting the Chester Valley. Many large and old trees may be seen in the vicinity of Paoli. It is not, however, until we reach the mountains farther west that the tree becomes sufficiently abundant to be used for tanning purposes.

Much confusion has occurred and probably exists at the present time concerning the various species of chest-

nut oaks. Michaux considered there were two species, *Q. Prinus palustris* and *Q. Prinus monticolor*. It

FIG. 3.



Quercus Prinus, L.
ROCK CHESTNUT OAK.

is doubtful, however, if there is any real difference, since the distinction appears to have been based solely

on the shapes of the leaves. There do appear two varieties of leaves, as shown in Figs. 3 and 4, but the difference is not greater than often occurs in some other species.

FIG. 4.

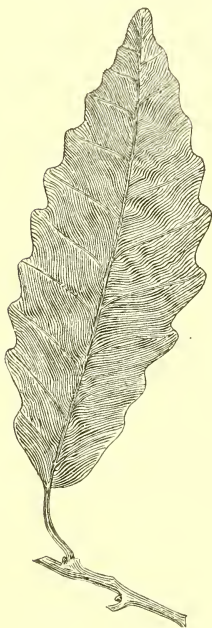
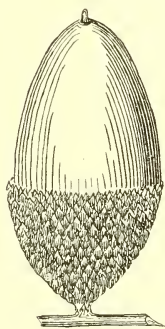


FIG. 5.



Quercus Prinus, L.

CHESTNUT OAK. ROCK CHESTNUT OAK.

The young and vigorous trees usually have leaves of the shape shown in Fig. 3, while the older trees, and perhaps those younger ones that are imperfectly nourished, have much narrower leaves, as shown in Fig. 4. The acorns (Fig. 5) and bark appear to be the

same for both varieties of leaves. The bark is rough, gray, and deeply furrowed. It becomes rough soon after the trunk attains a diameter of eight inches. The tree when full-grown often reaches a height of eighty to ninety feet, although when it grows in open spaces away from the influence of other trees it partakes more of the character of the white oak, by dividing into several large branches at a distance of ten or twelve feet from the ground.

In addition to the bark being valuable for tanning, the wood is considered next in value to the hickory for fuel. This statement was made by Michaux more than eighty years ago, and the same was recently made to the author by a farmer living in a district abundantly supplied with chestnut oaks, and where the inhabitants partly depend on wood for fuel. The coarse grain of the wood prevents its use for many purposes to which white oak is adapted, but it is still of great value for employment in many other ways.

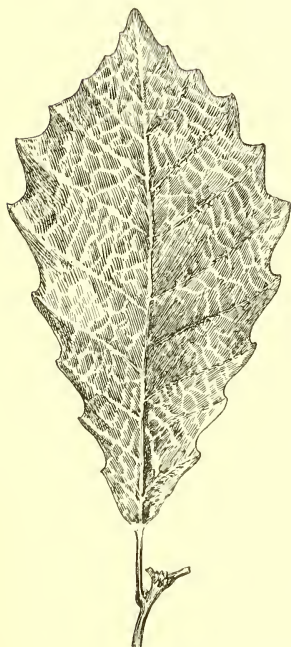
Closely related in appearance to the Rock Chestnut Oak is the Yellow Chestnut Oak, or *Quercus Muhlenbergii*, Engelm. This Michaux described as *Q. Prinus*, var. *acuminata*, and further stated that it was often confused with the preceding varieties. The Yellow Chestnut Oak is found from Massachusetts to Delaware, and along the mountains somewhat farther south; west it occurs as far as Eastern Nebraska, Minnesota, and Texas. It is not frequently seen in the East; one tree is known in the vicinity of Philadelphia, and that is situated about four miles north of Paoli in the Chester Valley. This particular tree was mentioned by Darlington in his "Flora Cestrica"

in 1835, and it is now (1894) a vigorous tree seventy to eighty feet in height and three feet in diameter. Its trunk is covered with a white flaky bark much re-

FIG. 7.



FIG. 6.



Quercus Muhlenbergii, Engelm.
YELLOW CHESTNUT OAK.

sembling that of the white oak. The foliage is composed of two varieties of leaves: on the lower branches they are broad (Fig. 6), while above (Fig. 7) they are narrower; they much resemble the leaves of the

FIG. 8.



Quercus bicolor, Willd.
SWAMP WHITE OAK.

two varieties of the Rock Chestnut Oak, although in this particular case the two kinds of leaves are on the same tree. The bark, acorns, and color of the wood

distinguish the *Q. Muhlenbergii* from the other species of chestnut oak. Regarding the color of the wood, it may be said that it is described as yellow in the books, but this color is not very marked; it becomes more decided when the wood is polished and varnished.

The Swamp White Oak, *Quercus bicolor*, Willd., in appearance and some other characters, stands between the Chestnut Oak and the White Oak. The leaf (Fig. 8) resembles the broad leaf of the Rock Chestnut Oak, while the bark is very similar to that of the White Oak, except that in some instances it is in much larger flakes. It is distributed over the United States as far south as Georgia, but is nowhere so abundant as to have any special use. It is sometimes employed in place of White Oak, and its wood is about equal in value with the wood of that species.

The *Quercus alba*, L., or common White Oak, is perhaps the most widely distributed and abundant of any of the American oaks. It is found from Canada to Florida and west to the Rocky Mountains. It is said to attain its greatest size on the western slope of the Alleghany Mountains. The tree is often eighty to one hundred feet in height and three to five feet in diameter. In forests the trunk often attains considerable height without branching, but when it is allowed plenty of room, as in open fields, it divides into a number of large branches at ten or twelve feet from the ground. The leaves are somewhat variable in shape—a very common type is shown in Fig. 9. The acorn is shown in Fig. 10.

The bark is thin and not so rich in tannin as that from some other species, and is, therefore, not much em-

ployed by tanners. It is, however, officially recognized as the only oak bark to be used in medicine. The

FIG. 9.



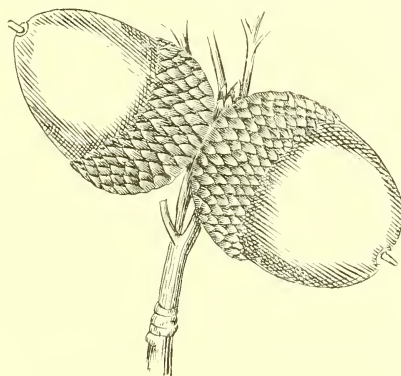
Quercus alba, L.
WHITE OAK.

wood constitutes the chief value of the White Oak. It is extensively employed in building, in the manufacture of furniture, and for fuel. Of all the American

oaks, this most closely resembles the European *Quercus robur*.

On account of its light-colored bark, the *Quercus virens*, Ait., or Live Oak, is usually classified with the above-mentioned species. It is found in the United States from Virginia southward, rarely, if ever, more than thirty miles from the coast, since salt air appears

FIG. 10.



Quercus alba, L.
WHITE OAK.

to be necessary to its existence. In its most northern habitat the Live Oak is rather small, but farther south it becomes one of the largest, as well as one of the most picturesque trees of the forest. The latter effect is much heightened by the moss (*Tillandsia usneoides*, L.) which usually covers the branches and hangs gracefully to a distance of several feet below them. The wood is yellowish in color, and, on account of its great strength

and durability, was formerly much prized for ship-building.

The bark is excellent for tanning, but is not much employed. This is no doubt due to the fact that little tanning is done in the localities where it flourishes. It may be interesting here to recall a prediction of Michaux in 1810, when, because of the many demands made on the Live Oak for ship-building, he said, "I cannot but consider its disappearance throughout the United States within fifty years as nearly certain." A journey at the present time, after the lapse of eighty years, through our south Atlantic coast States would reveal the fact that, of the Live Oaks in existence at that time, many are still standing, and others have grown to replace a great number of those that have been used. It is no doubt true that there are not nearly so many Live Oaks now as there were then, but it was at that time as it is now, unsafe to predict the time when our forests will disappear.

The following quotation from Bartram's "Travels in North America," 1793, is of interest as giving a good description of this tree, as well as some of its uses at that time: "The Live Oaks are of astonishing magnitude, and one tree contains a prodigious amount of timber. . . . The trunk of the Live Oak is generally from twelve to eighteen feet in girth, and rises ten or twelve feet erect from the earth,—some I have seen eighteen or twenty,—then divides itself into three, four, or five great limbs, which continue to grow in nearly an horizontal direction, each limb forming a gentle curve, or arch, from its base to its extremity. I have stepped above fifty paces, on a strait line, from the

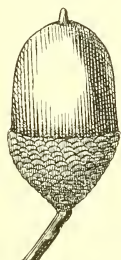
trunk of one of these trees to the extremity of the limbs. It is evergreen and the wood almost incorruptible, even in the open air. It bears a prodigious quantity of fruit; the acorn is small, but sweet and agreeable to the taste when roasted, and is food for almost all animals. The Indians obtain from it a

FIG. 11.

*Quercus virens*, Ait.

LIVE OAK.

FIG. 12.

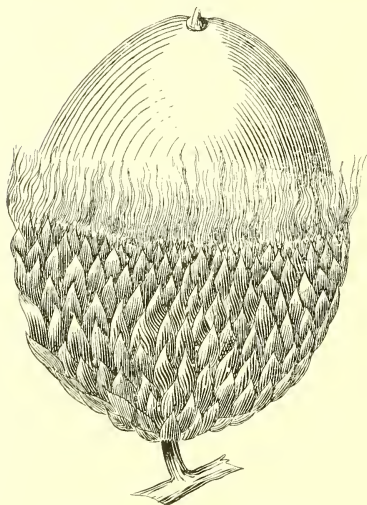


sweet oil, which they use in the cooking of hommony, rice, etc.; and they also roast it in hot embers, eating it as we do chestnuts."

The accompanying illustrations (Figs. 11 and 12), taken from Michaux, will give a sufficient idea of the leaf and fruit, natural size, to enable one to recognize the species.

Quercus macrocarpa, Michx., Bur Oak, Mossy-cup Oak, Over-cup White Oak, is a large and valuable tree found in the United States from Maine to Pennsylvania and thence westward to the Rocky Mountains. This oak is abundantly distributed through the Western prairie lands. One of its peculiarities is the readiness with which it adapts itself to nearly every climate in the United States. Michaux spoke rather disparagingly of it, but its wood is much prized by the farmers

FIG. 13.



Quercus macrocarpa, Michx.
BUR OAK. MOSSY-CUP OAK.

of the West, both for manufacturing purposes and for fuel. Its peculiar fruit and large leaves (Figs. 13 and 14) readily distinguish it. Michaux also called attention to its fruiting sparingly, but during a recent journey of the author through the States of Illinois and Iowa, a very different impression was received. In many instances trees were seen loaded with

acorns, with as many as six or eight crowded on the end of a single branch.

Quercus stellata, Wang., *Q. minor*, Marsh., *Q. obtusiloba*, Michx., Post Oak, Iron Oak, is found from

Massachusetts south and west. It is especially abundant in the southwestern section of the United States, and flourishes on barren and sandy soils. It attains a

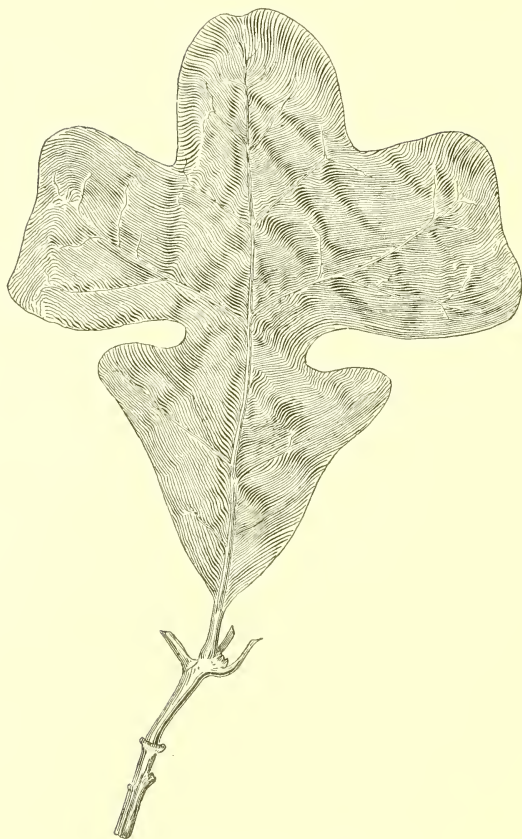
FIG. 14.



Quercus macrocarpa, Michx.
BUR OAK. MOSSY-CUP OAK.

height of from twenty to fifty feet, and yields a hard wood of considerable value on account of its durability. In general appearance the tree somewhat resembles the

FIG. 15.

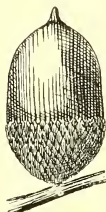


Quercus stellata, Wang.
POST OAK.

White Oak, but the leaves are thicker and more downy underneath. Fig. 15 represents the peculiar shape of the leaf by which it is readily distinguished. The acorn is shown in Fig. 16.

The Red, Scarlet, and Black Oaks are typical members of a group that have many natural points of resemblance.

FIG. 16.

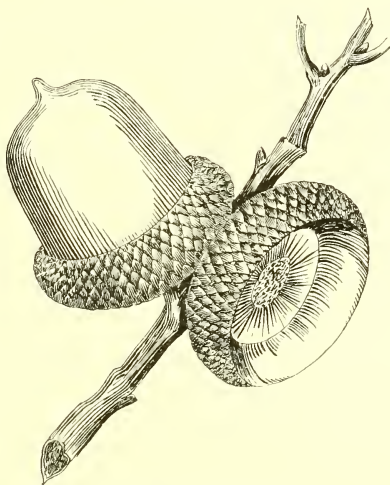


Quercus stellata, Wang.
POST OAK. IRON OAK.

is especially mentioned by one writer as occurring in the neighborhood of Bingen on the Rhine. Why it should have been preferred to the Chestnut Oak, which is much more highly prized in this country, is not clear. The acorns of the Red Oak readily distinguish the species by their peculiar flat saucer-shaped cups. (Fig. 17.) The tree frequently attains a height of eighty feet. Its wood is rather porous, and, although used considerably, is not esteemed so much as that from many

Quercus rubra, L., Red Oak, is widely distributed east of the Rocky Mountains. Its habitat is said to extend farther north than that of any other Atlantic oak. For some unaccountable reason this oak has been selected for cultivation in Germany. It

FIG. 17.



Quercus rubra, L.
RED OAK.

other species. The bark is used in tanning, and occasionally to correct the color imparted to the leather by the Black Oak. A practical difficulty in the way of using

FIG. 18.



Quercus rubra, L.
RED OAK.

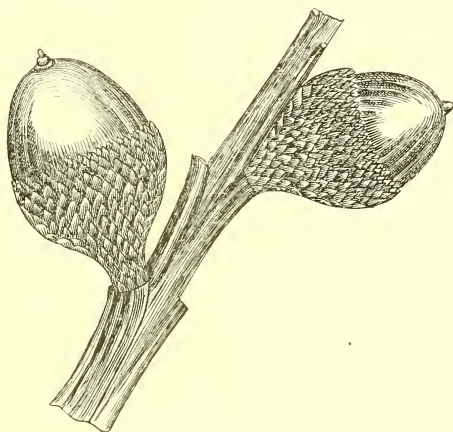
the bark is the resistance it offers to grinding, since when dry it becomes exceedingly hard and tough.

The foliage of the Red Oak bears a close resemblance

to that of the Black Oak, but lacks the peculiar gloss of the latter. The shape of the Red Oak leaf is shown in Fig. 18.

Quercus coccinea, Wang., Scarlet Oak and the Black Oak, *Q. tinctoria*, Bar., may be considered together, since Gray classifies the latter as merely a variety of the former. They are quite abundant in Northeastern United States, and extend well southward on the mountains.

FIG. 19.

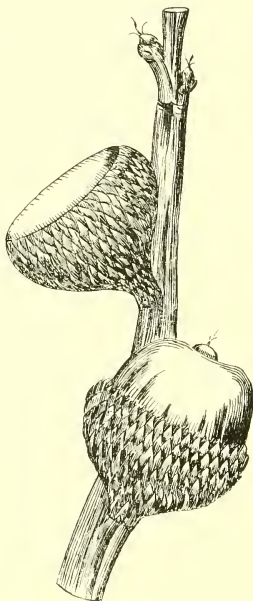


Quercus coccinea, Wang.
SCARLET OAK.

It is quite difficult to distinguish these two varieties by their general appearance. The leaves of the Scarlet Oak are more deeply lobed than those of the Black Oak; but this is a relative difference only, and therefore usually leaves a doubt in the mind unless the two varieties can be seen growing near together. The acorns of each bear a close resemblance. (Figs. 19 and 20.)

M i c h a u x states "that the only constant difference is in the kernel, which is yellowish in the Black Oak and white in the Scarlet." This appears not to be mentioned in any of the more recent works on the subject, and, while on close examination it is true, it requires

FIG. 20.



Quercus coccinea, var. *tinctoria*, Gray.

BLACK OAK.

that the acorns shall be nearly matured before the distinction becomes sufficiently apparent to be of value, consequently it applies to only a short period in each year. A test which may be applied at all seasons of the year is given by M i c h a u x as follows: "All doubt

may be removed by chewing a bit of the cellular tissue of each ; that of the Black Oak is very bitter and gives a yellow tinge to the saliva, which is not the case with the other." It will be found that the best cellular tissue for this purpose is obtained by removing a small piece of the inner bark from the trunk, since this is much richer in the coloring matter than that from the small branches.

The Scarlet Oak has a reddish inner bark, and this bark imparts no yellow color to the saliva ; it has a coarse gritty feel between the teeth, and is almost free from bitterness.

The Black is distinguished from the Red Oak by the same test for yellow coloring matter, but to certainly distinguish the Scarlet from the Red Oak we are compelled to rely on the differences in their acorns, or else judge by the surface of the leaf, which is smooth and glossy in the Black and Scarlet, but of rather a paler color in the Red. The shape of the leaf is a great help when we have a typical specimen, as in Figs. 21 and 22.

When grouped together in forests these Black Oaks become very large trees, with straight trunks running up a great height without a branch. Groves of these trees may frequently be seen in the vicinity of Philadelphia, which are now preserved for their ornamental beauty.

Bartram in his travels through Georgia, 1793, remarks on the stately Black Oaks as follows: "To keep within the bounds of truth and reality, in describing the magnitude and grandeur of these trees, would, I fear, fail of credibility, yet, I think, I can

FIG. 21.

*Quercus coccinea*, var. *tinctoria*, Gray.

BLACK OAK.

assert, that many of the Black Oaks measured eight, nine, ten, and eleven feet diameter, five feet above the ground, as we measured several that were thirty

feet girth, and from hence they ascend perfectly straight, with a gradual taper, forty or fifty feet to the limbs ;

FIG. 22.

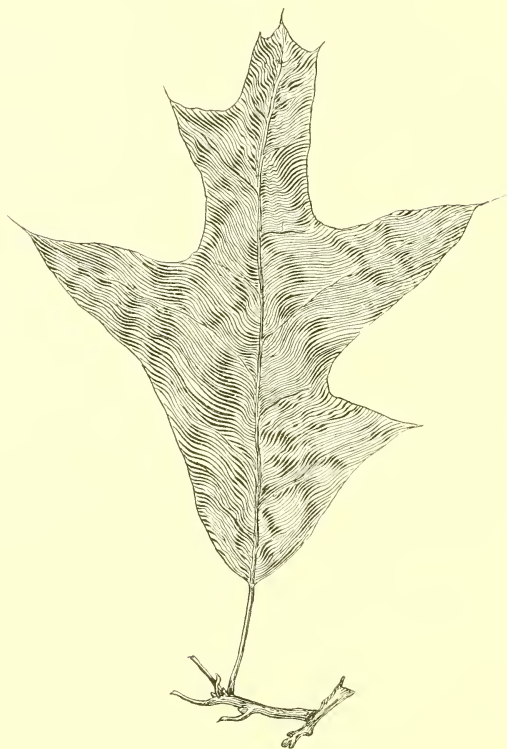


Quercus coccinea, Wang.
SCARLET OAK.

but, below five or six feet, these trunks would measure a third more in circumference, on account of the pro-

jecting jambs, or supports, which are more or less, according to the number of horizontal roots they arise from."

FIG. 23.

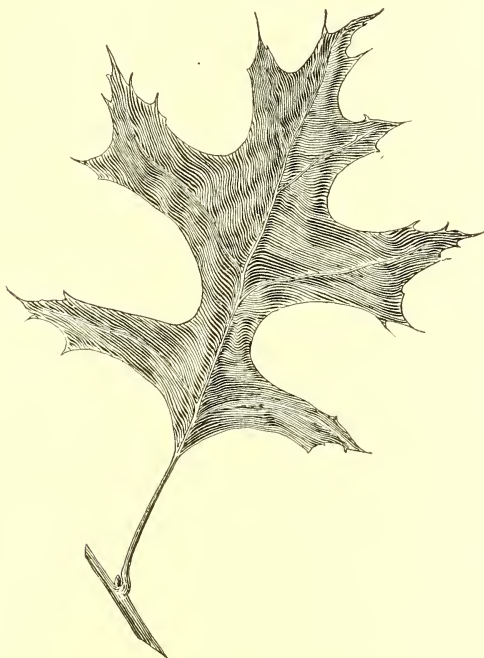


Quercus falcata, Michx.
SPANISH OAK.

The woods of the Black and Scarlet Oaks are considered more valuable than those from many other of the American species, but inferior to that of the European, *Q. robur*.

Quercus falcata, Michx., *Q. cuneata*, Wang., Spanish Oak, is frequently referred to as being excellent for tanning. It does not, however, appear to be so abundantly distributed as many of the other species.

FIG. 24.

*Quercus palustris*, Du Roi.

PIN OAK.

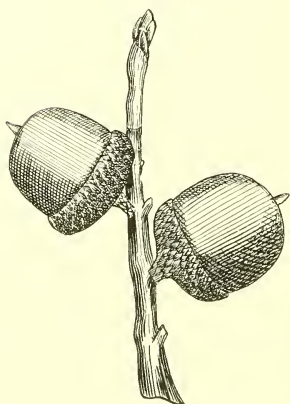
In the North it is rather small, but South it becomes a large tree, more abundant, and is much used. It is sometimes known in the latter section under the name of Red Oak. The leaves, as shown in Fig. 23, are sufficiently characteristic to distinguish it. The

bark, like that of the Red Oak, is said to be useful to mix with the Black Oak bark in order to correct the color of the latter. In connection with this, however, it may be said that the yellow coloring matter is also found in small proportion in Spanish Oak bark.

Quercus palustris, Du Roi, Pin Oak, Swamp Spanish Oak, is rather abundantly distributed in the North Atlantic States, and as far west as Kansas. In the latter locality it is frequently known by the inhabitants as Jack Oak. The Pin Oak is usually found in low ground, or along the banks of streams. It attains

its greatest size west of the Alleghany Mountains, where it often reaches a height of eighty feet. The tree is readily distinguished by its leaves (Fig. 24) and by the short branches usually covering the trunk. The wood is not especially valuable, and is not much used except in the absence of other species. The acorn is plump and of medium size, as shown in Fig. 25.

FIG. 25.

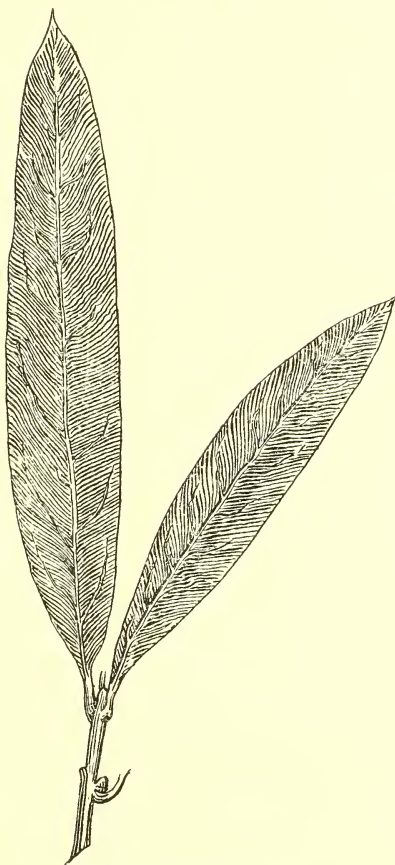


Quercus palustris, Du Roi.
PIN OAK.

Quercus Phellos, L., Willow Oak, is found in the Atlantic States

from New Jersey southward to Florida, and westward to Missouri and Texas. It possesses the foliage of the

FIG. 26.



Quercus Phellos, L.
WILLOW OAK.

willow (Fig. 26, natural size) with the fruit of the oak (Fig. 27). The bark is smooth, rather thick, and nearly free from corky layer. The tree does not usually attain

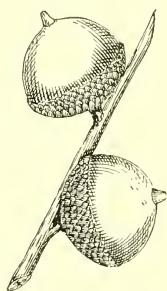
any notable size, and neither the bark nor the wood is considered of much value.

Of the oaks on the Pacific coast the author cannot speak from observation or personal experience, therefore will only briefly mention two that are held in considerable value in that region, on account of their abundance and for the value of their bark in tanning.

Quercus Kelloggii, Newberry,

Black Oak, is found in great profusion in Southern Oregon and California. It is especially distributed through the dense forests of the latter State. It reaches a height of eighty to one hundred feet and a diameter of three to four feet. The wood is heavy, hard, close-grained, and brittle, consequently is not much used except for fuel. The bark has considerable use in tanning.

FIG. 27.



Quercus Phellos, L.
WILLOW OAK.

It is the analogue of the Eastern Red Oak.

Quercus densiflora, H. and A., Tan Bark Oak, is abundantly distributed in California and Oregon; the greatest development being in the redwood forests of the California coast ranges. It attains a height of sixty to eighty feet and a diameter of two to three feet. The wood is valueless, and is only used for fuel. The bark is highly prized, and is used extensively for tanning, as its percentage of astringent principle exceeds that of any other Pacific oak.

It will, perhaps, be sufficient to enumerate by title

some of the other oaks occurring chiefly in Eastern United States. Few, if any, of these have come into prominence, probably because of their local distribution or scarcity. Many of them are, however, of rare scientific interest from a botanical stand-point, and all of them are waiting for the chemist to investigate their tannins.

Q. heterophylla, Michx., Bartram's Oak.

Q. lyrata, Walt., Over-cup Oak, Swamp Post Oak.

Q. Michauxii, Nutt., Basket Oak, Cow Oak.

Q. coccinea, var. *ambigua*, Gray, Gray Oak.

Q. illicifolia, Wang., Bear or Black Scrub Oak.

Q. aquatica, Walt., Water Oak.

Q. nigra, L., Black Jack or Barren Oak.

Q. imbricaria, Michx., Laurel or Shingle Oak.
(Figs. 28 and 29.)

It is with some regret that a more extended description of the various oaks cannot here be given, but it is kept in mind that the astringent principle is the special subject of this work, and only so much has been included in this section as may aid the investigator in properly comprehending the sources of the tannin.

The composition of the various oak barks has been but very little studied. Attention has usually been directed only to the one important constituent, tannin.

The analysis of oak bark most frequently quoted in text-books is that of Gerber in 1831. It is probable that his investigation was conducted on the bark of *Quercus robur*, since in Europe the bark of that species is usually understood when none is specified.

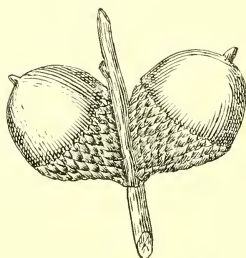
As long ago as 1864, Eckert declared the results

FIG. 28.



Quercus imbricaria, Michx.
LAUREL OR SHINGLE OAK.

FIG. 29.



Quercus imbricaria, Michx.
LAUREL OR SHINGLE OAK.

of Gerber to be “illusory and worthless” from a quantitative stand-point. They are, however, of some

historical interest, and, on that account, are quoted here, as follows :

Gallic acid contaminated with some tannin	1.09 per cent.
Gum contaminated with salts . . .	8.50 "
Tannin	5.60 "
Extractive, with sodium chloride, malic acid, salts, and some sugar .	8.33 "
Extractive	4.54 "
White resin	1.11 "
Wax-like fat	0.66 "
Red tannin extractive (oak red) .	2.34 "
Pectic acid	6.77 "
Calcium phosphate	0.40 "
Basic magnesium phosphate	1.15 "
Calcium and magnesium malate . .	0.80 "
Fibre	58.23 "
	99.52 "

In the year 1843, Gerber published some further results on his investigations of oak bark, in which he described the discovery of a bitter principle, to which he gave the name of *quercin*. This was obtained by extracting the bark with very dilute sulphuric acid, neutralizing with calcium hydrate, precipitating the excess of calcium by potassium carbonate, filtering, evaporating the filtrate to dryness, and extracting the quercin with alcohol. He found it to occur in small, white, odorless, and bitter crystals, easily soluble in water and diluted alcohol, but insoluble in absolute alcohol and ether. It had a neutral reaction, and was colored orange-yellow by sulphuric acid. This compound H u s e m a n n has since declared to be impure *quercite*, a peculiar sugar.

Stenhouse, about the same time, and during his experiments on *Quercus pedunculata*, decided that the tannin was different from that of nutgalls, and that no gallic acid was present.

In the light of these results, Eckert, in 1864, concluded that a new investigation was needed. The bark was collected in the spring of the year from a young tree two or three inches in diameter. Whether from *Q. robur* or *Q. pedunculata* he could not positively say. As the distinction is rather a nice one, it is perhaps true, as he stated, that it was not a matter of any practical importance.

Eckert extracted a portion of the bark successively with ether, absolute alcohol, water, and diluted hydrochloric acid. The first solvent dissolved about 1 per cent. of a resin-like substance; absolute alcohol extracted 6.1 per cent. of the bark, and with the remaining solvents he did not attempt any quantitative determinations. The tannin which was removed by alcohol gave a steel-blue precipitate with salts of iron, while that removed afterwards by water gave with the same reagent a dark-green precipitate. The tannin was shown to be different from that of nutgalls by investigating the lead salt; this confirming what Stenhouse had previously pointed out. Eckert was unable to find the bitter quercin discovered by Gerber. By using the same process he obtained sodium acetate. He did not, however, entirely discredit Gerber's results, but suggested that the bitter principle might be present in the bark of older trees. As stated above, Husmann appears to have disposed of this principle, although some American species, notably *Q. tinctoria*,

possess a very bitter taste that must belong to a peculiar substance.

Eckert completed the record of his results by a full statement of the mineral constituents, which, as they are somewhat inaccessible in the original, are introduced here.

The total amount of ash found was 5.175 per cent., constituted as follows :

Sodium chloride	0.5855	per cent.
Potassium oxide	5.3031	"
Sodium oxide	1.1013	"
Calcium oxide	48.0800	"
Magnesium oxide	4.3847	"
Aluminum oxide	0.0883	"
Ferric oxide	0.2836	"
Manganous oxide	1.7385	"
Sulphuric acid	0.4121	"
Phosphoric acid	3.1128	"
Silicic acid	0.3020	"
Carbon dioxide	34.4800	"
	99.8719	"

The proportion of tannin in the various oak barks has always claimed much attention. Beginning with *Quercus robur*, we find many different percentages given by as many different investigators.

Davy, in 1803, was among the first to make an estimation of the tannin in oak bark. He naturally used gelatin as the reagent for precipitating the tannin, of which he found 6.04 per cent. in the entire bark. In the interior white bark he found 15 per cent. by the same process.

Since that time hundreds of results have been recorded, and, notwithstanding the great variety of pro-

cesses employed, it may still be said that the percentage of tannin given has been, almost without exception, between the above figures of D a v y. P r o c t e r gives 10 to 12 per cent. as the amount in European oak barks.

A sample of fine quality Hereford Oak Bark—*Quercus robur*—recently received by me from Prof. P r o c t e r, yielded 6.39 per cent. moisture, 5.36 per cent. ash, and 12.37 per cent. tannin, calculated for absolutely dry substance.

Without attempting to detail the results of the various authors, it will, perhaps, be sufficient to take those of W e i s s, in 1885, which cover the various commercial varieties of Europe. He took fifteen samples, of which 1, 2, 3, were Hungarian; 4, 5, 6, were German; 7, 8, 9, were French; 10, 11, 12, were Danish; 13, 14, 15, were Swedish. The following are the percentages of tannin and ash obtained, based on absolutely dry substance :

	Tannin.	Ash.		Tannin.	Ash.
1	10.36	7.31	9	13.87	6.14
2	11.10	6.57	10	15.12	7.13
3	13.47	5.68	11	13.86	7.81
4	11.87	8.52	12	14.59	6.66
5	16.09	6.32	13	12.02	5.55
6	16.18	6.27	14	12.27	6.04
7	16.22	7.49	15	11.60	7.05
8	13.82	7.77	Mean	13 50	6.82

It is to be regretted that the species were not given by the author. The hide powder method was used.

There are four species in Europe that are usually found in commerce, *Q. pedunculata*, *Q. sessiliflora*, *Q. Cerris*, and *Q. pubescens*. Of these, the first are con-

sidered the best. Their tannin values were compared by E i t n e r in 1878, with the following results :

<i>Q. pedunculata</i> ,	collected during the last of April,	14.80	per cent.
<i>Q. sessiliflora</i> ,	" " " "	12.86	" "
<i>Q. pedunculata</i> ,	" " " May,	10.71	" "
<i>Q. sessiliflora</i> ,	" " " "	10.46	" "
<i>Q. pedunculata</i> ,	" " " June,	12.33	" "
<i>Q. sessiliflora</i> ,	" " " "	10.58	" "
<i>Q. pedunculata</i> ,	" " " July,	9.80	" "
<i>Q. sessiliflora</i> ,	" " " "	8.11	" "
<i>Q. pedunculata</i> ,	" " " August,	11.23	" "
<i>Q. sessiliflora</i> ,	" " " "	10.74	" "

It has been determined that various influences govern the percentage of tannin in oak-bark. The bark from trees on a poor dry soil is richer than that from trees grown in damp lowlands. W o l f f has shown that the more vigorous trees yield a higher percentage of tannin. In stems of the same age, the thickest yielded 15.26, the medium 14.04, and the smallest 13.43 per cent. tannin. All were fourteen to fifteen years old.

The inner bark is, of course, much richer in tannin than the dry outer corky layer. A mean of eighteen assays by W o l f f yielded 6.72 per cent. for the cork, and 14.43 for the inner bark.

It is generally conceded that the barks collected during the latter part of May and in June are the richest in tannin.

A more recent series of investigations on the percentage of tannin in the oak was made by E. H e n r y in 1888. He examined both the bark and the wood of oaks from two different districts in France, with the following percentage results of tannin in the material dried at 100° :

Sample.	Bark.	Sap-Wood.	True Wood.		
			Outer.	Intermediate.	Centre.
1 . . .	10.33	3.27	5.78	4.91	4.04
2 . . .	10.09	2.07	9.63	7.09	6.41

Unfortunately, he did not give the species of oak employed in this investigation. He further determined that the tannin occurs in greater proportion in the oaks grown in calcareous soils than in those grown in silicious soils.

The estimations of tannin in American oaks have been nothing like as numerous as those of the European species. Comparatively few have been recorded. The following percentages of tannin were obtained by the author from the bark of such American oaks as are found in Eastern United States. The hide powder process was employed. The estimations were made of the inner bark, or what is known as "rossed" bark; that is, after the corky layer had been removed. Most of the bark was gathered from comparatively young trees, and after air drying for a few days, the estimations were made at the same time that a portion was taken and dried at 110° to determine moisture. The tannin results were then calculated for the absolutely dry bark.

Species.	Date of Collection.	Per Cent. of Tannin in the "Rossed" Bark dried at 110°.
<i>Quercus palustris</i>	July, 1893.	7.60
<i>Q. Phellos</i>	December 25, 1893.	5.28
<i>Q. coccinea</i>	March 28, 1893.	8.61
" "	July, 1893.	5.86
<i>Q. tinctoria</i>	May, 1893.	11.01
" " (bark of root)	December 25, 1893.	7.55
<i>Q. rubra</i>	March, 1894.	4.04

Species.	Date of Collection.	Per Cent. of Tannin in the "Rosseed" Bark dried at 110°.
<i>Q. alba</i>	March 28, 1893.	6.96
<i>Q. falcata</i>	June 14, 1893.	10.23
<i>Q. stellata</i>	July 31, 1893.	7.70
<i>Q. bicolor</i>	July 31, 1893.	14.21
<i>Q. virens</i>	August, 1893.	3.91
<i>Q. Prinus</i>	December 12, 1892.	9.33
" "	March 28, 1893.	10.63
" "	June 14, 1893.	11.22
" "	July 31, 1893.	11.70
" "	September 20, 1893.	6.66

The constituents, other than tannin, of the American oak barks are probably not very different from those of the European species, except the coloring matter, which is closely associated with the tannin, and which appears to be different for nearly every species.

In *Q. tinctoria* and *falcata* it is the yellow quercitrin, while in the closely related *Q. rubra* and *coccinea* it is red. The most interesting and peculiar of these coloring matters is a fluorescent one in *Q. Prinus*, chestnut oak. In this, and probably in most other species, the blue color and precipitate with salts of iron are not caused by the tannin, but by the coloring matter. As will be shown later under the reactions, the purified tannins give a green color with iron salts instead of a blue one, as is generally stated in the books. A blue color with the salts of iron is obtained when we use an infusion of the bark.

Some experiments on chestnut oak bark demonstrated that the fluorescent coloring matter might be separate from the tannin by means of neutral lead acetate, which precipitated the tannin, but not the coloring principle.

This latter could then be precipitated by lead oxyacetate. So far, however, it has not been found possible to separate it from the lead compound and get it in a pure condition. The readiness with which it decomposes has been the cause of failure.

The coloring matter associated with the tannin of the willow oak, *Q. Phellos*, was likewise found to be different from that in all other species. These coloring principles alone are worthy of a special investigation.

It may be of sufficient interest to mention here a sample of oak bark recently received from Mr. A. E. Wild, of Dehra Dún, India, through the kindness of Mr. David Hooper. This sample was from *Quercus semicarpifolia*, known there as *Karshun*. It yielded 7.04 per cent. of moisture, 10.12 per cent. of ash, and 8.60 per cent. of tannin, calculated for absolutely dry bark. The composition and reactions of this tannin will be given in a later section of this volume.

SECTION II.

HISTORY.

To a certain extent the bibliography of oak tannin is a history. The titles of the contributions on the subject frequently furnish a clue to the contents.

The early history of this tannin is not separable from the general history of the whole subject in the first volume of this work. It may be of interest, however, to mention an early reference to the oak not there noted.

George Swayne, in 1792, communicated to the Society of Arts his results on the use of oak leaves in tanning. On account of the bulkiness of the leaves and the trouble and expense of drying them, he suggested that they be extracted with water, and the resulting solution concentrated to a suitable consistency. He then commented on the legal difficulties as follows : " But before the leaves can in any way be legally used by the tanner, it is necessary that the act of Parliament be repealed which confines him to the use of ash and oak bark. This restriction was probably laid, not solely from the belief that those substances were the most proper for the purpose of tanning leather, but likewise to encourage the planting and nurturing of those valuable timber-trees."

The act of Parliament recalls to mind the equally peculiar one, which prohibited the use of logwood as a

dye-material. We may also note that more than a century ago the cry was raised to spare the trees.

When Proust, in 1802, announced that there are many different kinds of tannin in different plants, he laid the foundation for the individual consideration of the various tannins, although future investigations will probably show that there may be a reduction of the great number of individuals to a few groups. There elapsed, however, many years, after Proust's work, before it was realized that the tannin of oak bark might be different from that of nutgalls.

Berzelius, in his *Lehrbuch*, 1827, used the term "*eichen-Gerbstoff*," and stated that "the whole species *Quercus* contains a tannin, which appears to be the same; it is found in the wood of the trunk and root, in the bark, in the leaves, and in the greatest abundance on the leaves of *Quercus infectoria*, formed through the sting of *Cynips quercusfolii* and occurring in commerce under the name of gall apples."

In the fifth edition of Liebig's *Handbuch der Chemie*, 1843, the name *eichengerbstoff* is credited to Berzelius, and there are given the synonymes *Gerbstoff*, *Acidum quercitannicum*, and *Tanningenium*. The following quotation indicates the views held at that time: "*Occurrence*: In the wood, root, bark, leaves, and especially the bark of all the oak species and many other plants. Very pure in nutgalls." It is quite certain that the tannin of oak bark had not been separated in a pure state at that time, but, on account of the blue color given by the infusion with salts of iron, it was assumed to be identical with that from nutgalls.

Stenhouse, in 1842, appears to have been the

first to squarely face the fact that nothing was known of any of the tannins except that prepared from nutgalls. The following quotation indicates that he realized some of the difficulties in the way: "It is much to be regretted that we are unable to procure tannin in a state of purity from any other source than nutgalls. When pounded galls are treated by Pelouze's method, with hydrated ether, in a displacement apparatus, the liquid on standing separated into two strata, the lowest of which contains tannic acid in a state of purity. When, however, oak bark, valonia, sumach, gum kino, catechu, etc., are treated with ether in a similar manner, only one stratum of liquid is obtained." He further showed, by operating on considerable quantities of oak bark and its extract, that neither gallic nor pyrogallie acid was produced.

The history of oak tannin for the next twenty-two years, from 1842 to 1864, shows that but little advancement was made in the knowledge of its composition and properties. This may have been partly due to the fact that it was slowly being realized by chemists that oak tannin was quite a different substance from gallotannic acid, and in greater degree to the fact that most chemists were absorbed in the progress made towards the better understanding of gallotannic acid.

In 1864, Eckert made some efforts in the preparation of a pure oak tannin by precipitating an infusion of oak bark with acetate of lead. His experiments on the lead salt obtained in this way, and purified, led to the formula $C_{28}H_{20}O_{20}.3PbO$.

Further attempts were made to obtain a pure oak tannin by Grabowski in 1867, under the direction

of Hlasiwetz. He noted that a watery decoction of oak bark was cloudy, and that, like an infusion of galls, it yielded tannin on the addition of sulphuric acid ; an important distinction, however, in the product was that the one from galls was easily converted into gallic acid, while that from oak bark yielded only traces of this substance, but instead there was produced in considerable quantity a red amorphous body which he designated *oak red*. He considered the best method of preparation to be that in which the decoction was fractionally precipitated by lead acetate, the lightest colored portions reserved, treated with hydrogen sulphide, and, after removal of the lead sulphide, evaporated to dryness. The tannin prepared in this manner was considered to be a glucoside, and its decomposition products were compared with those of some other tannins.

The year 1869 was marked by two important publications on this subject. One entitled *Die Gerbrinde* (The Tanbarks), a monograph of two hundred and forty-one pages, by J. G. Neubrand. This, however, is devoted more to forestry than to the tanning principle. The other, a monograph of forty pages, *Ueber den Gerbstoff der Eiche* (On the Tannin of the Oak), by Dr. Theodore Hartig. This is divided into two chapters: (1) On the nature of the tannin. (2) On the influence on the yield of tannin by the age of the tree, the season of the year, and the manner of cultivation. The work has been very widely quoted, and justly deserves to be, since it contains an account of a long series of investigations, extending over a considerable period of time, and involving a large number

of tannin estimations. The whole investigation involves important questions of plant physiology, which are of great interest, although the methods employed for estimating tannin, necessarily defective, made it impossible to deduce any laws showing the amount of tannin present at different seasons of the year.

Oser, in 1875, repeated some of Hartig's experiments without any more definite results. He also repeated the work of Grabowski, and attempted to prepare a pure oak tannin by the same process, namely, fractional precipitation with lead acetate. By concentrating the final tannin solution in a vacuum, he obtained a lighter colored product which, when dried at 100° under the same conditions, gave on analysis the following percentage composition :

Carbon	54.82
Hydrogen	4.57
Oxygen	40.61

corresponding to the formula $C_{18}H_{18}O_{10}$. By further drying at 120° in a stream of carbon dioxide, he obtained a product which, when submitted to analysis, gave the following :

Carbon	55.04
Hydrogen	4.59
Oxygen	40.37

corresponding to the formula $C_{20}H_{20}O_{11}$. Neither of these results corresponds with those obtained at the present day. He further attempted to arrive at the true composition of oak tannin by preparing and analyzing the cinchonine compound, but with indifferent success.

In the same year, 1875, there was published at Dorpat, Russia, the Inaugural Dissertation of Edwin Johnson. This was entitled "A Contribution to the Chemistry of the Oak, Willow, and Elm Barks." The practical part was conducted under the supervision of Dragendorff. This monograph of ninety-five pages comprises an account of the preparation and purification of the tannin from each of these three sources, the analysis of each, the effect of heat, acids, and alkalies on each, and the preparation and examination of a number of salts of each. The ultimate analyses of the oak tannin indicated the composition and formula assigned it by Wagner, namely, $C_{28}H_{16}O_{16}$. It may here be recalled that Wagner, in 1866, obtained this formula by the analysis of the cinchonine compound.

Johnson further showed that the three tannins agreed in many of their properties, but not in composition. The conclusion drawn by several subsequent writers has been that he decided the tannins were identical in composition; this, however, cannot be confirmed by a careful perusal of the original publication, although future investigations may show them to be the same.

Thus far the method of extracting the tannin had been almost exclusively by water, and subsequent purification by fractional precipitation with lead acetate.

Johnson experimented with 85 per cent. alcohol for extracting, but concluded that it had no advantages over water on account of the large proportion of resin which it removed with the tannin.

We now reach a new era in the history of this tannin, when either a solvent different from water was used in

extracting, or else acetic ether instead of lead acetate was recognized as a better agent for purification.

The investigations of this period refer chiefly to the composition and constitution of the oak tannin, although the methods of preparation are incidentally considered.

Those most prominently identified with the work, commencing in the year 1880 and extending to the present time, have been Etti, Löwe, and Böttlinger. Procter has been engaged particularly on the reactions and methods of estimating this as well as many other of the tannins, and has been especially successful in perfecting this branch of the subject.

The history of the oak tannins during this period naturally brings us to the present knowledge of the subject, which may be appropriately summed up here, although it must again be frequently referred to in the separate chapters on their preparation and their composition. The three authors, Etti, Löwe, and Böttlinger, have differed so widely among themselves, that at present it is impossible to harmonize their results.

Etti and Löwe both worked on the subject in 1880, but the publications of the latter do not appear until 1881. They, therefore, conducted their first investigations without criticism of each other, and, perhaps, without either knowing that the other was engaged in this work.

Etti continued his investigations, and published further results in 1883, 1884, and 1888. In his first communication in 1880 he made an important departure in the preparation of the tannin, by using a very dilute alcohol for extracting, and then separating the

tannin from this by agitation with acetic ether. In order to overcome the solvent power of the alcohol for the tannin, he first saturated the solution with ether, and then on agitating with acetic ether, the latter, he claimed, removed a larger quantity of the principle than would have been the case if the saturation with ether had been omitted. On concentrating the acetic ether solution and allowing it to stand for some time, ellagic acid crystallized out and was separated by filtration. The filtrate was evaporated to dryness on a water-bath, and yielded a reddish-white powder, which consisted of the oak tannin, a little phlobaphene, some amorphous resin, and a small quantity of gallic acid. The last two substances were removed by treating this residue with absolute ether so long as anything was removed. The phlobaphene was extracted from this residue by repeated treatment with a mixture of three parts of acetic ether and one part of ordinary ether, both free from alcohol. This mixture dissolved the tannin and left the phlobaphene. The product obtained from the evaporation of these two ethers was considered pure oak tannin.

From six kilogrammes of the parenchyma portion of the oak bark there were obtained four decigrammes of gallic acid.

The oak tannin prepared as above was described as a "reddish-white" powder, soluble in alcohol and very dilute alcohol, insoluble in ether, and insoluble, or only very slightly soluble, in water. This property of insolubility in water is an unaccountable peculiarity of Etti's oak tannin, and will be referred to again. It was necessary, therefore, in order to apply the ordi-

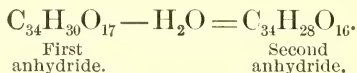
nary tests to this tannin, to use a solution in very dilute alcohol. The reactions then agreed closely with those of other investigators. It should be particularly noted here that he obtained a blue color and precipitate by adding a solution of this tannin to a solution of ferric chloride. The solution of this tannin, he stated, could be evaporated to dryness on a water-bath without undergoing decomposition, provided no alkali or mineral acid were present. It did not decompose when heated to 130° , but between that temperature and 140° it commenced to lose weight, with the formation of an anhydride, which was the product from two molecules of the tannin losing one molecule of water. The tannin, when dried below 130° , yielded the following percentage composition by elementary analysis :

Carbon	56.31	56.06
Hydrogen	4.63	4.69

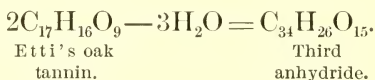
From these results he deduced the formulas $C_{17}H_{16}O_9$ and $C_{19}H_{18}O_{10}$.

The former he has adhered to. To the anhydride he assigned the formula $C_{34}H_{30}O_{17}$. This anhydride he claimed to be present in the oak bark, and that it remained in the dilute alcoholic extract of the same after agitation with acetic ether. It was recovered from this by diluting with water, although it still retained inorganic matter ; by redissolving in alcohol and reprecipitating, by pouring into water containing some dilute hydrochloric or sulphuric acid, a product was obtained free from ash, which on analysis indicated the same formula, $C_{34}H_{30}O_{17}$, as that obtained by heating the tannin above 130° . This he called the *first* anhydride.

By heating this for some time with dilute sulphuric or hydrochloric acid he obtained a *second* anhydride, having the composition represented by the formula $C_{34}H_{28}O_{16}$, derived from the first anhydride by the loss of one molecule of water, as follows :



When the original tannin was treated with dilute sulphuric acid (1-20) it dissolved, and on boiling for some time a red precipitate was formed. This collected, washed, and dried formed the *third* anhydride, derived by two molecules of the tannin losing three molecules of water :



This third anhydride Etti considered identical with Oser's oak red. He further prepared an oak phlobaphene, by boiling the tannin for some time with a dilute solution of potassium hydrate and precipitating with an acid.

The above anhydrides were found to be insoluble in water, but soluble in alcohol and in dilute solutions of the alkalies. They colored solution of ferric chloride blue.

By a series of experiments, too long for repetition in a general history, Etti proved that oak tannin was not capable of yielding glucose, and, therefore, could not be a glucoside. This was, perhaps, the first positive statement of this fact backed by careful experiment,

and Löwe reached the same conclusion independently and at about the same time. From eighty grammes of the tannin Etti obtained one and a half grammes of gallie acid. He concluded that a methyl radical existed in the tannin, because he observed the peculiar flame of methyl chloride when he ignited the gas formed on heating oak tannin with concentrated hydrochloric acid in a sealed tube. On fusing fifteen grammes of the tannin with five times its weight of potassium hydrate, and, after cooling, acidifying with sulphuric acid, he obtained 0.35 gramme of protocatechuic acid, 0.2 gramme of catechol, and traces of phloroglucol.

Etti concluded at the close of this investigation that oak tannin might be derived from gallotannic acid by replacing three hydrogen atoms of as many hydroxyl radicals by three molecules of methyl.

Löwe differed somewhat from Etti in his method of preparing oak tannin, although he used acetic ether. He extracted the bark with 90 per cent. alcohol, concentrated this extract with exclusion of air, and poured the syrupy residue into eight or ten parts of water. After allowing it to stand for some time, he separated the clear liquid, and saturated it with pure common salt. The treatment with water separated resin and insoluble anhydride, and the salt separated additional anhydride. The clear filtrate from the latter was agitated with ether to remove gallie acid, and then with acetic ether, which removed the tannin. Ellagic acid was found along with the gallie acid in the extraction with ether. The several extractions with acetic ether were mixed and the solvent recovered by distillation, the residue was treated with water and allowed to stand

for several days, when it was filtered and the filtrate concentrated in a desiccator over sulphuric acid.

The product was of a cinnamon-brown color and dissolved clear in water. Its solution gave precipitates with tartar emetic, gelatin, and the alkaloids, and colored the salts of iron bluish-black. The average of eight analyses of this product, dried without heat over sulphuric acid, gave in per cent. :

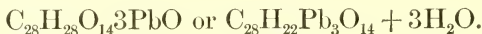
Carbon	55.422
Hydrogen	4.631

This, Löwe concluded, corresponded to the formula $C_{25}H_{30}O_{15}$ or $C_{28}H_{28}O_{14} \cdot H_2O$.

An additional quantity of oak tannin was prepared by Löwe from an aqueous extract of the bark, by precipitating with 90 per cent. alcohol, allowing to stand until the precipitate subsided, then separating the clear liquid, and treating it as in the preceding process. The product was not only dried over sulphuric acid at the ordinary temperature, but was then brought to a temperature of 120° in an air bath. The mean of fourteen analyses gave the following :

Carbon	56.835
Hydrogen	4.372

corresponding to the formula $C_{28}H_{28}O_{14}$ or $C_{28}H_{24}O_{12} \cdot 2H_2O$. He prepared and analyzed the lead salt by precipitating the alcoholic solution of lead acetate with an alcoholic solution of the tannin. The product on analysis gave the formula :



On account of its behavior with dilute acids, Löwe, like Etti, decided on the non-glucosidal nature of this tannin.

In addition to the above there were separated and examined an anhydride of the composition $C_{28}H_{24}O_{12}$, having a lead salt of the composition $C_{28}H_{22}PbO_{12} \cdot 3H_2O$, and an oak red having the composition $C_{28}H_{22}O_{11}$.

The history of the year 1880 would be incomplete unless reference were made to the work of Böttinger on phlobaphene and oak red. He first reviewed the history of these two principles, which are so closely associated with oak tannin, and we find that the first reference to phlobaphene was made by Stähelin and Hofstetter in 1844.

Böttinger prepared phlobaphene by first removing fat and wax from oak bark with ether, then exhausting with alcohol, and evaporating the resulting extract slowly on a water-bath. The residue, he said, consisted essentially of two substances, one of which—oak tannin—was easily soluble in water, and the other—phlobaphene—was insoluble in that liquid.

The phlobaphene he found would dissolve in warm water (more readily in the presence of oak tannin) and deposit from a dilute solution in a brown powder.

The oak red he prepared by decomposing a moderately concentrated solution of the tannin with sulphuric acid. He considered that phlobaphene and oak red were identical, because "both possessed the same physical and chemical properties, and behaved similarly towards oxidizing agents, zinc dust, fused potassium hydrate, acetic anhydride, benzoyl chloride, and fuming hydrochloric acid." The following percent-

age results of elementary analyses confirmed this view :

	Phlobaphene dried at 108°.		Oak red dried at 108°.		
	I.	II.	III.	IV.	V.
Carbon	59.86	59.93	60.19	60.08	59.79
Hydrogen . . .	4.47	4.12	4.22	3.94	4.40

These results are best expressed by the formula $(C_{14}H_{10}O_6)_2H_2O$.

This phlobaphene was found to be insoluble in water and in cold alcohol, somewhat soluble in these liquids when hot, and readily soluble in dilute aqueous solutions of the alkali hydrates. To salts of iron it imparted a black color. By the action of fused potassium hydrate it yielded protocathechuic acid and phloroglucol.

Böttiger gave much time and space to the problem of the constitution of phlobaphene, and concluded by saying that as tannic acid may be considered the anhydride of carboxylpyrogallol, so the phlobaphene may be considered the anhydride of methyl and carboxylpyrogallol.

In Etti's second communication in 1883 he first reviewed his previous work and maintained its correctness, then compared his own results with those of Böttiger and Löwe. At the same time he published the result of a further investigation on an oak bark furnished by W. Eitner. From this he obtained a tannin identical in all respects with the one previously prepared by him, except that it gave a green color with salts of iron instead of a blue, and it had the composition corresponding to the formula $C_{20}H_{20}O_9$ instead of $C_{17}H_{16}O_9$, which represented the former one. This dif-

ference Ett i failed to account for unless it were due to the second sample of bark having been obtained from a different species of oak. About this time, W. Eit ner, who furnished the second sample, published in *Der Gerber* his views on this subject, in which he stated that the first sample investigated by Ett i was obtained from *Quercus robur*, while the second sample was from *Quercus pubescens*.

Eit ner, however, failed to comprehend why Ett i should have obtained a tannin insoluble in water, for he likewise had prepared a tannin from the bark of this species and had found it readily soluble in water. It is unaccountable that 0.6 part of Ett i's tannin should have required 100 parts of water to dissolve it.

This statement of solubility he repeated in the second communication, so that it could not have been due to a typographical error. At this time, Ett i called attention to the fact that oak tannin decomposed acetic ether like a mineral acid, and that the resulting acetic acid acted on the tannin, converting a portion of it into oak red. He, therefore, employed the following method of extraction: The powdered parenchyma of the bark was exhausted with 20 per cent. alcohol. To the filtered liquid so much ether was added as was required to saturate the liquid and form a layer above, several centimetres high. The ether was then separated and distilled, and the operation repeated until benzol ceased to remove any more green resin from the ether residue. The liquid which had been exhausted with ether still contained some green resin which was removed by diluting with water and filtering. The filtrate was agitated with benzol to remove the

last traces of resin. The liquid was then diluted with some weak alcohol, and the whole carefully treated with small portions of lead acetate, until a pure yellow precipitate was obtained, by which means anhydrides were removed. The filtrate from this was agitated with ether containing some alcohol, which removed the oak tannin. The operation was repeated so long as any of the tannin was removed. The collected ethereal liquids were distilled to remove the ether, and the residue was evaporated on a water-bath and dried at 105° . An ultimate analysis gave :

	Found.			Calculated for $C_{20}H_{20}O_9$.
	I.	II.	III.	
Carbon . . .	59.21	59.10	59.56	59.40
Hydrogen . .	5.06	4.95	4.96	4.96

This communication of Etti was followed in the same year, 1883, by a rejoinder from Böttiger. Without attempting to prepare a pure tannin the latter proceeded at once with the bromine compound, by acting on a watery extract of oak bark with bromine. In this manner he obtained a light yellow precipitate, which he found to be easily soluble in alkalies, ammonia, aniline, acetic ether, alcohol, and especially a mixture of ether and alcohol. The composition of this substance he found to correspond to the formula $C_{19}H_{14}Br_2O_{10}$, consequently he named it dibrom oak tannin. This was converted, when heated to 80° with acetic anhydride, into pentacetyl-dibrom oak tannin, which was found to be soluble in dilute alkaline liquids. By careful addition of bromine the dibrom oak tannin was converted into tetrabrom oak tannin, $C_{19}H_{10}Br_4O_{10}$; this likewise was found to be capable

of conversion into a pentacetyl compound, when heated with acetic anhydride to 80° .

In conclusion, Böttiger proposed $C_{19}H_{16}O_{10}$ for the formula of oak tannin, and considered that it must be a condensation product of an oxygen-bearing aldehyd, $CH_3CH_2-CO-CH_2-CHO$, with gallotannic acid.

In a communication the next year, 1884, Böttiger changed this statement, on account of having detected the methyl radical, to the opinion that it was a methyl ether of the condensation products of acetoacetaldehydes with gallotannic acid.

He further, in this latter paper, investigated the compounds of bromine with a number of tannins. These compounds were prepared by saturating infusions of the various tannin-bearing materials, which as far as possible had been prepared in the cold, with bromine. When the latter was shown by the color to be in slight excess, the resulting precipitates were allowed to settle, then collected, washed with water, at first containing sulphurous acid, afterwards pure water, and finally dried over sulphuric acid at the ordinary temperature. When the bromine was estimated in the precipitates, there resulted three groups according to the percentage, as follows:

I.	II.	III.
Oak bark, 28.00 p. c.	Hemlock bark, 43.60 p. c.	Mimosa, 49.36 p. c.
	Quebracho wood, 44.50 "	Chestnut oak, 50.48 "
	Mangrove bark, 42.15 "	Terra Japonica, 53.20 "
		Larch bark, 52.80 "

These precipitates were not soluble in ordinary ether, although they deliquesced when in contact with it. They dissolved in alcohol and in glacial acetic acid.

The balance of this paper was devoted particularly to the acetyl derivatives of some of the bromine compounds, and to the anhydrides, but not to oak bark tannin.

In 1887, Böttiger published two communications on this subject. The first referred especially to oak wood tannin, and the second to the tannin from oak bark. He found that the infusion of the wood did not yield a precipitate with bromine, as was the case with that of the bark. He, therefore, prepared the acetyl compound by taking commercial oak wood extract, dissolving it in twenty parts of water, and allowing it to stand until a clear supernatant liquid had formed. This clear solution he decanted and evaporated to dryness. The dry extract was powdered and treated with acetic anhydride, the result being an acetyl compound, which was separated from coloring matter by dissolving in glacial acetic acid and pouring into water, which precipitated the product in a partly pure condition, a repetition of the process resulted in a pure compound. This acetyl compound was found to be insoluble in water, ether, and alcohol, but soluble in acetic ether, chloroform, and acetone, and to have the composition represented by the formula $C_{15}H_7(C_2H_3O)_5O_9$. On heating this with water in a sealed tube to 135° there resulted acetic acid and a red-brown powder, the anhydride of oak wood tannin. This powder was collected, washed with water, dried at a temperature not exceeding 25° , dissolved in alcohol, evaporated, the residue dissolved in water, and evaporated to dryness in a desiccator over sulphuric acid. Thus formed it was a light brown powder, hygroscopic and easily sol-

uble in water or alcohol. Its percentage composition corresponded to the formula $C_{15}H_{16}O_{11}$, but on heating to 135° it lost two molecules of water, so that the formula became $C_{15}H_{12}O_9 \cdot 2H_2O$. A monobrom derivative of the monoacetyl oak tannin was formed having the formula $C_{15}H_{10}Br(C_2H_3O)O_9$, and a tetrabrom derivative of the same having the formula $C_{15}H_7Br_4(C_2H_3O)O_9$. He considered that this oak wood tannin was a methyl ether of digallic acid, with an essentially different constitution from gallotannic acid.

In his communication on oak bark tannin he arrived at the conclusion that it possessed the empirical formula $C_{19}H_{16}O_{10}$. This was found to be capable of forming a bromine compound having the formula $C_{19}H_{14}Br_2O_{10}$, in which five hydrogen atoms were replaceable by acetyl. The tannin contained the group $COOCH_3$, and at least one easily eliminated hydrogen atom united directly with carbon.

In 1889, Etti reiterated his previous statements concerning a tannin from *Quercus robur*, L., having the composition represented by the formula $C_{17}H_{16}O_9$, and one from *Q. pubescens*, W., $C_{20}H_{20}O_9$, and that they were ketone acids, derived from a substance named by him *gallylgallic acid*, having the constitutional formula $C_6H_2(OH)_3CO \cdot C_6H(OH)_3COOH$, and isomeric with gallotannic acid. He also gave an account of another tannin obtained from the wood of the Slavonian stalk oak, "Stieleiche." It was prepared from the commercial extract by diluting the latter with water, allowing to stand several hours, separating the clear liquid, and treating it with concentrated hydrochloric acid as long as any precipitate was produced. The

clear liquid was syphoned from the precipitate, and the latter washed with water until free from hydrochloric acid, and then dried. The dry substance was dissolved in 95 per cent. alcohol, filtered, and the filtrate treated with $1\frac{1}{4}$ volumes of water to precipitate additional resin which was filtered out, and the filtrate evaporated to dryness. If the residue dissolved in 40 to 45 per cent. alcohol, it was considered pure, if not, it was treated with alcohol of this strength, the insoluble portion filtered out, and the filtrate evaporated to dryness, which yielded the tannin in a pure condition. This tannin was found to have the composition $C_{16}H_{14}O_9$, and was considered to be a dimethyl derivative of a ketone acid. Still another tannin was isolated by Etti from the bark of an unknown species of oak, which he found had the composition expressed by the formula $C_{18}H_{18}O_9$.

Etti concluded that the ketone tannins occur in plants as easily soluble magnesium salts. This theory enabled him to account for the ease with which most tannins are extracted by water, and after extraction and treatment with hydrochloric acid they become insoluble. To strengthen this view he prepared a number of magnesium salts of the tannin $C_{16}H_{14}O_9$.

This concludes a brief summary of the most important contributions on oak tannin since 1880. They are all long, and are scattered through a number of chemical journals, all in the German language. It is a tedious and laborious process to extract the facts from the original sources and to retain them clearly in the mind. If the above history fails to enable the reader to grasp the subject easily, the following chart may be of some assistance.

HISTORY.

Investigator.	Date.	Origin.	Method of Preparation.	Percentage Composition Car- Hydro- gen.	Formula.	Solubility in Water.	Behavior towards Ferric Chloride.
Böttlinger.	1883.	Unknown species of oak bark.	Treatment of aqueous infusion with bromine.	Calculated 56.43 3.96	$C_{10}H_{16}O_{10}$	Soluble.	Blue.
	1887.	Unknown species of oak bark.	Treatment of aqueous infusion with bromine.	Calculated ¹ 56.43 3.96	$C_{10}H_{16}O_{10}$	Soluble.	Blue.
	1887.	Commercial oak wood extract.	Decomposition of acetyl compound.	Calculated 48.55 4.42	$C_{12}H_{16}O_{11}$	Soluble.	Blue.
Löwe.	1880.	Unknown species of oak bark.	Extracted with 90 per cent. alcohol, saturated with salt, agitated with acetic ether.	Found ² 55.42 4.63 Calculated 55.44 4.95	$C_{22}H_{30}O_{15}$	Soluble.	Blue.
	1880.	Concentrated aqueous extract.	Precipitated with 90 per cent. alcohol and treated as above.	Found ³ 56.83 4.37 Calculated 57.14 4.76	$C_{23}H_{28}O_{14}$	Soluble.	Blue.
	1880.	Quercus robur, L.	Extracted with 20 per cent. alcohol, agitated with acetic ether.	Found ⁴ 56.18 4.66 Calculated 56.04 4.40	$C_{17}H_{16}O_9$	Insoluble.	Blue.
Etti.	1883.	Quercus pubescens, W.	Extracted with 20 per cent. alcohol, agitated with ether-alcohol.	Found ⁵ 50.29 4.99 Calculated 50.40 4.96	$C_{20}H_{20}O_9$	Insoluble.	Green.
	1887	Commercial oak wood extract, chiefly from Q. pedunculata.	Precipitated with hydrochloric acid.	Found 54.67 4.07 Calculated 54.85 4.00	$C_{16}H_{14}O_9$	Insoluble.	Blue then green.
	1887.	Unknown species of oak bark.	Not given.	Calculated 57.14 4.76	$C_{18}H_{18}O_9$	Insoluble.	Green.

¹ Dried at ordinary temperature over sulphuric acid.

² Dried at 100°.

³ Dried at 120°.

⁴ Dried below 130°.

⁵ Dried at 105°.

No reference in this summary has been made to a paper on oak wood tannin put forth by Böttiger in 1891. The contribution, however, is devoted to a number of reduction products of this tannin, and, while it is useful and interesting, it does not directly contribute to our knowledge of the tannin.

A criticism of the work done since 1880 has so far been avoided, but now, with the preceding chart in view, some opinions on this work may be of interest and in part account for the differences among those who have been engaged in the work.

It will be noticed that the choice of a source of the oak tannin was made in the most haphazard manner. Böttiger says nothing about the origin of the material from which his tannin was prepared until 1887, when he employed commercial oak wood extract. This extract was probably made from a number of species of oak, and the bark was no doubt extracted with the wood, since it is the custom of extract manufacturers to chip wood and bark together. The latter has but little value except for tanning; it is not probable, therefore, that the expense of removing it was incurred.

Löwe, in like manner, says nothing about the species of oak from which his material was obtained, and the best we can do is to suppose that it came from *Quercus robur*, L.

Etti published the results of two investigations, apparently without knowing what kind of oak bark he was using, until Eitner came to his rescue with a statement concerning the origin of the materials employed. Etti also depended on a commercial oak wood extract for his tannin from that source.

It does not appear to much purpose that these authors published so many pages of elaborate arguments concerning the constitution of the oak tannins, and severely criticised one another, when no one of them was able to say anything positive about the origin of his material, and no two of them derived their tannins from the same source. If it is true that all the species of oaks yield the same tannin, which may some day be shown, then we must look to some other source for the cause of their disagreement.

It is now known that the tannin from chestnut, *Castanea vesca*, is different from that of the oak ; therefore ever so small an admixture of this, which in the case of the commercial extracts is quite probable, would suffice to vitiate the results.

It has been the experience of the author of this volume that nothing short of going to the trees himself, or sending a trained assistant, will guarantee the genuineness of a material on which months of labor are to be expended.

The methods of preparation adopted by these three authors have in no case been the same ; therefore we could hardly look for exact agreement of results. The processes of Löwe and Etti are superior to those of all previous investigators, but when their descriptions are carefully followed, we find that in the preparation of tannin, an amorphous substance, they have scarcely employed as many purifications as are customary in obtaining a pure crystalline compound. Etti has repeated his belief in the correctness of the formula assigned by him to the tannin from *Quercus robur*, L., $C_{17}H_{16}O_9$, although he claimed that the process employed

by him was defective, and he adopted a different method for his second oak tannin, $C_{20}H_{20}O_9$.

Of the percentage composition obtained by these authors, and the formulas derived therefrom, little need be said at present. The temperature at which the tannin was dried during its preparation is given in some cases, but, with the exception of Löwe, we are left to infer the condition when weighed for combustion. In most cases, however, it has been possible to find the temperature at which the substance had dried before combustion, and these have been noted in the preceding summary.

The experience of all writers on this subject is so at variance with that of Etti, in regard to the solubility of the oak tannin in water, that it tends to cast a doubt on all his work. The author of this volume has found the tannin from *Q. robur* less soluble than that from other species, but not so insoluble as claimed by Etti.

Etti was, no doubt, right in finding that oak tannin gave a green color with ferric chloride, but he did not offer any explanation for the blue color which almost invariably occurs between the infusion of oak bark and the ferric salt.

It may now be said that it was useless to encumber this volume with a long historical account of work which has been so readily condemned, because of the uncertain origin of the materials used as a source of the tannin and of the faulty method by which the latter was prepared. The author, however, is inclined to believe that we cannot but derive benefit from a careful study of this work and strive to improve on it.

These men were far in advance of all previous investigators of this subject, and it now remains for us to endeavor to improve on them.

The history of oak tannin would be incomplete without some further reference to its anhydrides or "reds." It has been the intention thus far to say but little concerning them, for fear of falling into the same error as those who have previously given this subject their attention. As might be expected from the preceding remarks on the disagreement of authorities on oak tannin, there is a still more hopeless discrepancy among the same writers on these anhydrides.

Etti claims there are four of these anhydrides, and, in his communication of 1883, he has restored something like order out of chaos by constructing a chart of the results of Böttiger, Löwe, and himself, by which he makes the theory of the four anhydrides very plausible, especially as he at the same time incorporates a few corresponding results from the earlier writers.

The present author, however, makes one reservation, and that is, that in studying the original papers of the above-mentioned writers, so many compounds have been noted having a composition of from 50 to 60 per cent. carbon and 3.50 to 5.00 per cent. hydrogen, that it could not have been difficult for Etti to find enough agreeing with his own results to support his theory. In this, as in the oak tannin, before we can hope to arrive at exact knowledge of the subject we must be sure of the material on which we are working.

Chart of Oak Anhydrides by C. Etti, 1883.

		Calculated.		Found by Etti.			
1st Anhydride, C ₃₄ H ₃₀ O ₁₇ . Phlobaphene. Grabowski's Oak red.	}	Carbon,	57.46	57.28		57.62	
		Hydrogen,	4.22	4.64		4.69	
2d Anhydride, C ₃₄ H ₂₈ O ₁₆ .	}	Carbon,	58.96	58.76			
		Hydrogen,	4.04	4.20			
				Found by			
3d Anhydride, C ₃₄ H ₂₆ O ₁₅ . Oser's Oak red.	}	Carbon,	60.58	Oser.	Böttiger.		Etti.
		Hydrogen,	3.86	60.70	60.19	60.08	60.33
				4.03	4.22	3.94	4.03
				Found by Löwe.			
4th Anhydride, C ₃₄ H ₂₄ O ₁₄ . Löwe's Oak red.	}	Carbon,	62.20	62.339		62.197	61.997
		Hydrogen,	3.66	4.154		4.015	4.056

SECTION III.

PREPARATION AND PURIFICATION OF THE OAK TANNINS.

THE first attempts at preparing a pure oak tannin were the application of the lead acetate process ; that is, by extracting with water, and then precipitating the infusion with lead acetate in fractions, in which the middle portion was assumed to be pure. This precipitate was decomposed by hydrogen sulphide, and the filtrate from lead sulphide, after agitation with ether, was evaporated to dryness.

This was about the process of E c k e r t, G r a b o w s k i, and O s e r. Later, J o h a n s o n tried, besides this method, one in which he exhausted the bark with 85 per cent. alcohol, but concluded that the latter had no advantages as a solvent because it extracted so much resin along with the tannin.

In 1880, E t t i resorted to a very dilute alcohol as a solvent, but extracted the tannin from the solution by agitating with acetic ether instead of precipitating with lead acetate. L ö w e about the same time employed 90 per cent. alcohol as the menstruum for extracting, and then removed the solvent by distillation under reduced pressure. The residue he poured into eight or ten volumes of water and allowed to stand. The clear supernatant liquid he separated and saturated with common salt. This treatment separated anhydrides,

which were removed by filtration, and the clear filtered liquid was then agitated with ether to remove resinous compounds and decomposition products. After separation of ether the residual liquid was agitated with acetic ether, which removed the tannin.

Experiments have also been made with commercial ether as a solvent. This consists of about three parts ether, one part alcohol, and a little water. In addition to its slow solvent action, this menstruum is expensive, unless a substance contains over 10 per cent. of tannin; consequently only the richest oak barks could be profitably extracted by it. Acetic ether has also been suggested as a solvent, on account of the readiness with which it dissolves tannin, but its expense precludes it.

Recently, acting on a suggestion from Mr. George M. Beringer, the author has found a liquid which is cheaper than ether, and in addition is a more penetrating solvent, very rapid in its action.

This solvent is acetone. It extracts very little sugar and other carbohydrates. On account of its low boiling point, 56° , one is able to recover it by distillation while subjecting the dissolved tannin to a moderate temperature.

It has been tried with good success on the bark and wood of a number of American oaks, and the following general process has been adopted, to which has been added an account of the special experience with each species. Except where especially noted, the inner bark alone was used in these experiments. In all cases the bark was air-dry.

The powdered substance was well moistened with acetone, packed in a glass percolator, and the men-

struum poured on until it commenced to drop from the lower orifice, when the latter was tightly closed and the whole allowed to macerate for forty-eight hours. Enough of the solvent was poured on before maceration commenced to keep a thin layer of it above the drug. A glass plate smeared with petrolatum was kept on top of the percolator to prevent evaporation. At the expiration of the maceration period the stopper was removed, and the percolation continued rapidly until the number of litres of percolate amounted to one-half the number of kilogrammes of oak bark used. The latter was then usually found to have been exhausted. Water was then poured on the bark to displace the retained acetone. In every case the acetone rapidly penetrated the drug and accomplished complete exhaustion.

Percolation proceeded rapidly in every instance, no matter what the degree of fineness of the powder or the condition of the packing.

The acetone was removed by distillation, the first portion on a water bath, under ordinary conditions, but the last portion by the additional aid of reduced pressure. The residual product was in most cases warmed with water until nearly all of it dissolved; in a few cases alcohol of specific gravity 0.975 was used, which had the effect to lessen the formation of anhydrides.

After cooling, the whole was filtered, and the clear filtrate was diluted with water so long as a precipitation took place. This dilution separated the greater part of the anhydrides as well as some other coloring matter. The filtrate from these was of a clear red color and yielded no further precipitate on the addition of water. It was then agitated successively with acetic ether.

The acetic ether portions were mixed, and the solvent recovered by distillation under reduced pressure, which yielded the tannin in a porous or "puffed up" condition.

The product was then treated with cold water. When the amount of insoluble matter was small, paper pulp was stirred in to facilitate clarification. After filtration, the tannin with some coloring substance was again separated by agitation with acetic ether. This process was repeated until the tannin was readily and completely soluble in water. The tannin then possessed considerable odor of acetic ether, which was removed by solution in ether of the specific gravity 0.750, and, after filtering clear, distilling off the solvent under reduced pressure. The product was then digested with absolute ether, which dissolved the small amounts of adhering resin and crystalline principles occurring along with it in the bark, or resulting from decomposition during the process of extraction and purification. On removal of the absolute ether by distillation, completed under reduced pressure, the tannin was obtained in as pure a condition as it was possible to obtain it, and was readily and completely soluble in water.

This process was carried out on the barks from the following species of oaks, and the various modifications required by the presence of different coloring matters are explained in detail.

Quercus alba, White Oak.—The dark red acetone extract separated some red-brown phlobaphenes when treated with very dilute alcohol, specific gravity 0.975. A trial was made with a modification of the general purification process, in which the first acetic ether resi-

due was dissolved in water and filtered through a freshly prepared compound obtained by precipitating a portion of the aqueous solution of the residue with lead acetate. The filtrate was no lighter in color than the solution of the tannin before this treatment, and was not so clear. The finally purified tannin of this species was of a straw-yellow color.

Quercus coccinea, Scarlet Oak.—The reddish-brown acetone extract separated considerable anhydrides when treated with water, and, on filtering, a porous reddish tannin was removed from the filtrate by agitation with acetic ether. Further purification by solution in water and again shaking out with acetic ether gave a straw-yellow product.

Quercus coccinea, var. *tinctoria*, Black Oak.—On exhausting the bark with the same solvent employed in the preceding experiments, a dark red extract was obtained. When this was treated with alcohol, specific gravity 0.975, a large percentage of yellow substance, consisting presumably of quercitrin, was left undissolved. The tannin from the first acetic ether agitation was porous, yellow, and almost entirely soluble in water, with which the whole yield was treated. The filtered liquid was shaken with acetic ether. The latter was separated, and, upon standing overnight, deposited considerable yellow substance resembling that separated from the extract when previously treated with weak alcohol, and consisting, no doubt, of quercitrin. This deposition was allowed to go on until no further sediment was formed. The separation of this yellow substance did not much diminish the color of the tannin.

Quercus falcata, Spanish Oak.—The dark-colored

acetone extract from this species was treated with weak alcohol, as in the case of the *Q. tinctoria*; and the brownish substance which separated had the general characters of the quercitrin which separated from the bark of that species. This residue was treated with water, whereby some phlobaphenes were separated. The clear filtrate yielded to acetic ether on agitation with it, and distilling the latter, a porous, yellow tannin and much yellow coloring matter. This mixed product was completely dissolved in water and again shaken out with acetic ether. The acetic ether layer was separated and allowed to stand in order to allow the deposition of the yellow quercitrin. Although some of this material separated, the color of the resulting tannin was not much improved.

Quercus palustris, Pin Oak.—Besides considerable phlobaphenes which were colored dark green by the chlorophyll present, some waxy and fatty substances were left undissolved when the dark green acetone extract was treated with water. After repeated solution in water and shaking out with acetic ether, the tannin was obtained as a reddish-yellow product. In this case the modification of the purification process employed with *Q. alba* (filtration of the aqueous solution through a precipitate obtained by precipitating some of the infusion with lead acetate) was tried with more success than with the former species. The resulting tannin was nearly pure white in color, and the lightest shade of any of the oak tannins.

Quercus Prinus, Chestnut Oak.—The acetone extract from the bark of this species was red-brown in color. On treatment with alcohol, specific gravity

0.975, some phlobaphenes were left undissolved. The filtrate was diluted with water, which caused the separation of small quantities of anhydrides.

The clear reddish filtrate yielded to acetic ether a light reddish-yellow tannin, completely soluble in water.

Quercus bicolor.—A small lot of the bark of this species was exhausted with acetone. The dark amber extract on treatment with water yielded some phlobaphenes. The tannin finally obtained was reddish in color.

Quercus stellata.—The bark of this species gave a result similar to that of the preceding.

Quercus Phellos, Willow Oak.—The greenish acetone extract from the “unrossed” bark when treated with water separated some green and sparkling substance along with the phlobaphenes. The tannin obtained from the filtrate by shaking out with acetic ether was of a pale yellow color. The lead acetate process of purification was tried on this specimen as follows. When brought in contact with lead acetate a bright yellow color was produced, and the filtrate was more highly colored than the original solution was before the addition of the reagent. The lead tannate was thoroughly saturated with hydrogen sulphide in order to decompose the lead compound. After filtering and warming to expel the gas, the tannin was removed from the filtrate by means of acetic ether. The color was the same as before this treatment. In some experiments lead sulphide appeared to act as a decolorizer, but in this instance it was not a success.

Quercus rubra, Red Oak.—The bark of this species was subjected to the general process, without treatment

by the lead acetate, but only a small quantity of a red-brown tannin was obtained.

Quercus Prinus extracted by Acetic Ether.—The air-dry inner bark was moistened with acetic ether, and, after allowing it to macerate for forty-eight hours, it was percolated with the same solvent.

The acetic ether was recovered under reduced pressure, and a friable, porous, yellowish residue obtained. When this was treated with a large quantity of water much phlobaphene was separated. After filtering, the clear red filtrate was shaken with acetic ether, which removed a porous, yellowish tannin. The treatment was repeated until all the tannin was readily soluble in water and was of a straw-yellow color. After thorough drying at 120° , it was treated with absolute ether to remove decomposition products, and dried under reduced pressure on a water bath, which left it in a porous condition.

A sample of English oak bark, *Quercus robur*, mentioned in Section I. of this volume, was percolated with acetone similarly to the preceding species. The whole or "unrossed" bark was used. A very dark, reddish-brown percolate resulted. The extract, after removal of acetone by distillation, was nearly all soluble in weak alcohol, specific gravity 0.975.

The clear filtrate from the undissolved resinous products was agitated with acetic ether, but the latter solvent did not remove tannin as freely as was the case with the previous species. The tannin thus removed was of a dark red-brown color, even after further purification, and was not very soluble in water.

The weak alcoholic solution, which had been treated with acetic ether, still contained considerable tannin ; it was, therefore, precipitated with lead acetate, and the lead precipitate decomposed with hydrogen sulphide. After removal of lead sulphide, the filtrate refused to yield anything to acetic ether, it was, therefore, treated with a small quantity of acetone and saturated with common salt ; acetic ether then extracted a large proportion of the tannin, which was purified in the usual manner. The purified tannin was very dark brown in color, and was not as soluble as that obtained from the other oak species.

A previously mentioned sample from Dehra Dún, India, the bark of *Quercus semicarpifolia*, was extracted with acetone, and the solvent recovered by distillation. The residue of this acetone extract was nearly all soluble in water, and the aqueous solution, after filtration, yielded the larger proportion of its tannin to acetic ether. This tannin, after further purification by the usual process, was of a light, reddish-yellow color, and completely and readily soluble in water.

SECTION IV.

PROPERTIES AND COMPOSITION OF THE OAK TANNINS.

THE appearance of the oak tannins is dependent on the species from which the individual is derived. Each one is associated in the oak with a coloring matter, which in many cases belongs to that species only. For instance, in the *Quercus Prinus*, Chestnut Oak, it is a fluorescent principle. In the *Q. tinctoria* and *Q. falcata* it is quercitrin, and in some other species it is a red coloring.

So far it has been impossible to get an absolutely white tannin from the sources investigated. The color is lightest in the tannin of *Q. palustris*, Pin Oak, which in a porous condition is nearly white, and then the shade darkens through the various species to a dark, reddish-brown in *Q. robur*. The most difficult to purify are those tannins associated with quercitrin. No tannin, not even gallotannic acid, is white in color, unless it is in a porous condition; therefore it is necessary to get it in this state before a proper conclusion can be reached in regard to the shade of color. If such a porous tannin be powdered, it still retains the light color, since the physical condition is that of minute scales; therefore in speaking of the color it is understood to be of the tannin in a porous or powdered state.

The taste is astringent, with a faint bitterness; this bitterness probably belongs to lingering traces of another principle.

The odor is scarcely perceptible, and is quite likely to have resulted from the solvents used in extraction.

All of the oak tannins are soluble in water. This appears to have been the experience of all investigators, except Etti. It is simply impossible to account for his statement that the oak tannin prepared by him was insoluble in water.

With all other solvents, as with water, the oak tannins appear to have the same behavior as gallotannic acid ; that is, soluble in ether containing alcohol, in alcohol, glycerin, acetic ether, and acetone ; insoluble in perfectly absolute ether, chloroform, benzol, petroleum ether, and carbon disulphide.

The behavior of the oak tannins towards various reagents is practically the same for each. The slight differences noted among those from the various species are readily accounted for by the small amounts of adhering coloring matter.

The reactions have been studied of eight species of American oaks, of one English, *Q. robur*, and one from India, *Q. semicarpifolia*. Alongside of these were conducted the reactions of a sample of pure gallotannic acid. The tannin solutions were of $\frac{1}{2}$ per cent. strength. Some of these reagents were suggested by Procter in a paper on "The Testing of Tanning Materials," read by him before the World's Congress of Chemists at Chicago, August 25, 1893, and published in the *Proceedings of the American Chemical Society*, vol. xvi.

The results given by him apply to infusions of the tanning material, and not to the pure tannin, therefore they differ considerably from those noted in the following chart :

Reactions of Oak

REAGENT.	Black Oak, <i>Q. tinctoria</i> .	Pin Oak, <i>Q. palustris</i> .	Scarlet Oak, <i>Q. coccinea</i> .	Spanish Oak, <i>Q. falcata</i> .
Copper sulphate and Ammonium hydrate. }	Ppt. Green color.	Very slight ppt. Brownish-green color.	Ppt. Green color.	Ppt. Red-brown ppt.
Pine-wood shaving and hydrochloric acid.	Violet color.	Violet color.	Violet color.	Violet color.
Stannous chloride and hydrochloric acid.	Yellow color with some pink.	Pink color.	Pinkish color.	Yellow color with some pink.
Sodium sulphite.	Yellow color.	Pink color.	Pinkish-yellow color.	Yellow color with streaks of pink.
Nitrous acid.	Brownish-yellow ppt.	Pinkish color changing to brown ppt.	Brown ppt.	Brown ppt.
Bromine water.	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.
Ferric chloride and Ammonium hydrate. }	Green color and ppt. Purple-brown ppt.	Green color and ppt. Purple-brown ppt.	Bluish-green color and green ppt. Purple-brown ppt.	Green color and ppt. Purple-brown ppt.
Ammonio-ferric sulphate.	Green color and ppt.	Green color and ppt.	Bluish-green color and green ppt.	Green color and ppt.
Lime water.	Ppt. turning pink, then red.	Ppt. turning pink, then red.	Ppt. turning reddish.	Ppt. turning reddish.

Bark Tannins.

White Oak, <i>Q. alba.</i>	Willow Oak, <i>Q. Phellos.</i>	Chestnut Oak, <i>Q. Prinus.</i>	Swamp White Oak, <i>Q. bicolor.</i>	English Oak, <i>Q. robur.</i>	Indian Oak, <i>Q. semi-carpifolia.</i>	Gallotannic Acid.
Ppt.	Ppt.	No ppt.		Ppt.		No ppt.
Brown-green color.	Red-brown ppt.	Greenish-brown color.		Red-brown ppt.		Brown ppt.
Violet color.	Violet color.			Violet color.	Violet color.	Slight green color.
Pinkish color.	Very yellow color but no pink.			Decided pink color.	Pink color.	No change in color.
Pinkish color.	Yellow color with streaks of pink.			Pink color.	Yellow color.	Very slight pink color.
Brown ppt.	Brown ppt.			Pink color changing to brown ppt.	Brownish-yellow ppt.	Brown ppt.
Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.	Yellow ppt.	No ppt.
Green color and ppt.	Green color and ppt.	Green color and ppt.	Green color and ppt.	Bluish-gr'n color and gr'n ppt.	Green color and ppt.	Blue color and ppt.
Purple-brown ppt.	Purple-brown ppt.	Purple ppt.	Purple ppt.	Purple-brown ppt.	Purple-brown ppt.	Purple ppt.
Green color and ppt.	Green color and ppt.			Bluish-gr'n color and gr'n ppt.	Green color and ppt.	Blue color and ppt.
Ppt. turning pink.	Ppt. turning gr'n, liquid reddish.	Ppt. turning pink.	Ppt. turning pink.	Ppt. turning pink.	Ppt. turning pink.	Ppt. turning blue

One of the most important lessons to be learned from the preceding chart of reactions is, that the oak tannins give a green color and precipitate with salts of iron, instead of a blue one as is generally stated in the books. No doubt the blue color which oak infusions give with iron salts is due to an associated coloring matter. It was stated in a previous section of this volume, and it is here repeated, for emphasis, that in some cases this iron-bluing principle may be separated from the tannin by an appropriate reagent; in the Chestnut Oak, for example, it was possible to separate it by precipitating the tannin with neutral lead acetate, filtering, and afterwards separating the iron-bluing coloring matter with lead oxyacetate. No doubt in some of the other species, notably *Q. robur*, the same procedure might be successful.

Such reagents are omitted from the preceding chart as give the same reaction through the whole list of iron-bluing and iron-greening tannins, notably potassium bichromate, gelatin, and the lead salts.

DECOMPOSITION PRODUCTS.

Action of Heat.—About 0.5 gramme of tannin from each of the following species was taken: *Q. tinctoria*, *Q. palustris*, *Q. falcata*, and *Q. Phellos*. The samples in each case were heated with a few cubic centimetres of glycerin to 160° for twenty minutes, then the temperature was gradually raised to 190° for a few minutes. On cooling, each was agitated with successive portions of ether, the different portions of ether mixed and evaporated. There remained from each specimen a residue of square prismatic crystals, indicating catechol.

The residues were easily soluble in water, and the watery solutions were in each case tested with the following reagents. The differences were so unimportant that one result is here tabulated, as fairly representing the general conclusion :

Calcium hydrate . . .	Brownish-green or reddish color, becoming a ppt.
Ferric chloride	Brownish-green or green color.
Ferric acetate	“ “ “ “
Ferrous sulphate . . .	No change.

These reactions indicate catechol to be the chief decomposition product.

Action of Acids.—Two grammes of tannin from each of the following species were taken: *Q. tinctoria*, *Q. palustris*, *Q. coccinea*, *Q. falcata*, *Q. bicolor*, *Q. stellata*. The sample in each case was heated with 100 cc. of hydrochloric acid, 2 per cent. (absolute gas), at the boiling temperature for two and a half hours, during which time an amorphous, reddish-brown substance separated. The solutions were filtered, the insoluble substance washed with water and dried in the air.

The red-colored filtrates were separately shaken with several portions of ether, which removed a colorless crystalline substance.

The aqueous liquids, after agitation with ether, were warmed to expel the latter. After cooling, an excess of sodium acetate was added to each, and all were precipitated with lead oxyacetate. The mixtures were filtered, the lead removed from the filtrate by hydrogen sulphide, and the excess of the latter removed by warming. The clear filtrates were made alkaline and treated with Fehling's solution. With the *Q. palustris*

and *Q. coccinea* the reductions of this reagent were slight, but in the cases where there exists coloring matter, like quercitrin, associated with the tannin, there was a greater formation of cuprous oxide. The product from two species, *Q. bicolor* and *Q. stellata*, gave no reduction with Fehling's solution. These results appear to indicate that where the oak tannins are obtained in a state of purity there is no formation of glucose by hydrolysis, consequently they are not glucosides.

The crystalline principles mentioned above as having been extracted by stronger ether were found by the following reactions to be protocathechuic acid :

Ferric chloride	}	 Green color.
and		
Sodium carbonate	}	 Red color.
Ferrous sulphate		
Ammoniacal silver nitrate		Violet color.
Lead acetate		Reduced.
Lead acetate		Whitish ppt., the filtrate not ppt. by lead oxyacetate (absence of phloroglucol).

Action of Fused Alkali.—Some of the tannin from each of the following species was taken for the fusion : *Q. alba*, *Q. coccinea*, *Q. palustris*, *Q. Phellos*, *Q. robur*, *Q. tinctoria*, and *Q. falcata*. Each sample when added to the fused alkali dissolved with efferevescence and developed an odor similar to that noticed in soap-making. No such odor was obtainable from the fused alkali previous to adding the tannins. After the fusions had cooled the masses were dissolved in water, whereby clear solutions were obtained. These solutions were slightly acidified with dilute sulphuric acid, and the unfiltered solutions agitated with ether, which extracted

some crystalline substance. The crystals were found to be protocatechuic acid by the following tests :

Ferric chloride	}		Green or brownish-green color.
and			
Sodium carbonate	}		Red color.
Ferrous sulphate (neutral)		. . .	Violet or brownish-violet color.
Ammoniacal silver nitrate		. . .	Reduced.
Fehling's solution			Reduced.
Lead oxyacetate			Ppt.
Lead acetate			Ppt., filtrate not ppt. by lead oxyacetate (absence of phloglucon).
Pine wood and HCl			No violet or red color.

COMPOSITION.

The following are the results obtained by submitting the oak tannins to elementary analysis. Each sample previous to combustion was dried at a temperature of 120°.

	<i>Q. Prinus.</i>	<i>Q. coccinea.</i>	<i>Q. tinctoria.</i>	<i>Q. falcata.</i>	<i>Q. palustris.</i>
	Average	Average	Average	Average	Average
	of 2.	of 2.	of 3.	of 2.	of 2.
Carbon	59.69	59.58	58.87	59.95	61.26
Hydrogen	5.06	4.97	4.97	5.04	5.12
Oxygen	35.25	35.45	36.16	35.01	33.62
	100.00	100.00	100.00	100.00	100.00
	<i>Q. Phellos.</i>	<i>Q. alba.</i>	<i>Q. robur.</i>	<i>Q. semicarpifolia.</i>	
	Average	Average	Average	Average	
	of 2.	of 3.	of 2.	of 1.	
Carbon	57.67	61.19	59.77	60.15	
Hydrogen	5.06	5.15	5.14	5.19	
Oxygen	37.27	33.66	35.09	34.66	
	100.00	100.00	100.00	100.00	

This gives the average composition of the tannins from the nine species as follows :

Carbon	59.79
Hydrogen	5.08
Oxygen	35.13
	100.00

The extremes for carbon are 57.67 and 61.26, and for hydrogen 4.97 and 5.19. The higher figures represent the light-colored tannins from *Q. palustris* and *Q. alba*, while the low ones are those found to be associated with minute quantities of coloring matter, as in *Q. Phellos* and *Q. tinctoria*.

The author believes these results should be looked at as a whole and the average taken. When one has experienced the difficulties of purifying a plant compound for elementary analysis, that is crystalline, he can appreciate that the purification of an amorphous substance will require still greater care, and will be surrounded with many more difficulties. The materials for the above analyses were in most cases redissolved and separated seven or eight times, but the associated coloring matters so resembled the tannins in many of their properties that the two were only separated by much labor and loss of material.

It is a delicate point to decide when to cease purification; if not carried sufficiently far, adhering coloring matters remain, while, on the other hand, there is no doubt but slight decomposition may occasion a greater error.

Having summed up the results of elementary analysis on a number of oak tannins, it is in order to revert to our history. We find but two investigators have gotten results on the composition of the oak tannins corresponding to those above given. First, Etti obtained percentages agreeing fairly well with those found by me, but his carbon 59.29 and hydrogen 4.99 were only the results on the tannin from *Q. pubescens*. In the second instance, K r a e m e r, in 1890, obtained from

the tannin of *Q. alba*, carbon 59.65 and hydrogen 4.65. Considering the fact that he used quite a different method of preparation and purification from that employed by me, the results certainly are close for an amorphous substance.

It may here be stated that some of my own tannins were prepared and purified by a process different from the general one given, yet the results on combustion were practically the same. This was notably the case with the tannin from *Q. robur*, two samples being prepared by different methods, but the percentages of carbon and hydrogen respectively closely agreed in the two.

In the face of apparent failures by previous investigators to establish a formula for oak tannin, the author will not attempt to offer one at the present time. The one assigned to the tannin from *Q. pubescens* by Etti, $C_{20}H_{20}O_9$, is sufficiently near to the percentage results obtained by me to be accepted, but investigation on this subject must progress considerably before any formula will be needed.

SECTION V.

ESTIMATION OF THE OAK TANNINS.

MANY suggestions of improvements have been made since the general process for estimating the tannins as given in Volume I. of this work was published.

The method there laid down, consisting of the combined use of hide powder and potassium permanganate, as suggested by the Commission of German technical chemists in 1885, is, no doubt, used considerably at the present time. It is not, however, free from defects; besides being rather cumbersome and tedious, the results by this process are not such as to enable one to compare different tanning materials. In the present volume, however, the discussion will be confined to the assay of oak bark. The same precautions should be observed with this material in regard to sampling that were stated in Volume I.

Twenty grammes of powdered bark are placed in a Von Schroeder apparatus, covered with 200 cc. of water and heated in a boiling water bath for one-half hour. The piston covered with thin muslin is then pushed in, and the clear liquid poured into a litre flask. The extraction is then repeated, with 200 cc. of water at a time, until one litre of infusion is obtained. At this point the permanganate process may be abandoned and a modification of that with hide powder be followed,

in which the objections mentioned in Volume I. have been overcome by the improvements suggested by Procter. As modified by this author, the infusion is percolated through hide powder to remove tannin, rejecting the first 30 cc. of percolate, which contain the soluble matter of the hide. By evaporating portions of the infusion, before and after percolation, and subtracting, the difference will give the true value of the material for tanning purposes.

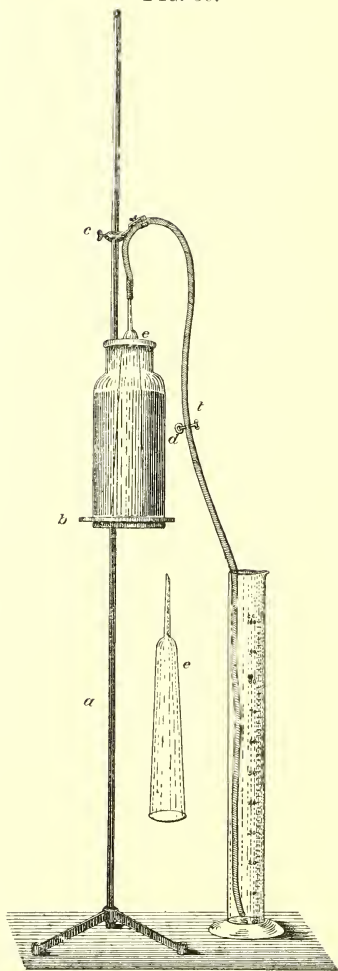
The apparatus for this process is so simple that almost every chemist can construct his own from the supplies in his laboratory. Procter recommends a glass tube in which the hide powder is placed, and the whole set in a beaker of the infusion. The clear liquid which rises up through the powder is syphoned off.

The apparatus illustrated in Fig. 30 has been used by the author of this volume with satisfactory results.

It consists of an ordinary retort stand, *a*, with one clamp, *c*, and one ring, *b*; on the latter a thin block of wood or metal is placed to support the bottle *d*. This bottle should be about 13 cm. in height and have a capacity of 400 to 500 cc. A small percolator, *e*, 18 cm. in total length and 2.5 cm. diameter at its wide end, some small size rubber tubing, and a graduated cylinder, make up the outfit. The glass percolator is the only piece of apparatus not found in every chemist's laboratory. It is easily made by almost any glass-blower; or a piece of glass tubing, fitted with a cork and tube, may be used, as suggested by Procter.

In using the apparatus the percolator *e* is fitted with a loose plug of absorbent cotton, pushed lightly down to the shoulder. Hide powder is then loosely dropped

FIG. 30.



in, and shaken moderately until eight or ten grammes have been used, and the powder is within 3 cm. of the top. Another plug of absorbent cotton is then placed in the open end sufficiently firmly to support the powder when the percolator is inverted. The latter is then connected with the rubber tubing and placed in the bottle *d*. The tubing is run up through the clamp *c* so as to give it a good curve and prevent it from bending and stopping the flow of liquid.

The infusion of bark is next poured into the bottle, a little at a time in order to moisten the powder by capillary attraction, rather than by pressure. When the bottle and percolator

are both filled, suction is applied to the open end of the rubber tubing very gradually, so as not to cause

the powder to pack. As soon as sufficient liquid has been drawn into the tube to cause the latter to act as a syphon, the open end is lowered into the cylinder. The first 30 or 40 cc. should be rejected, as they contain some soluble matter of the hide powder. 50 cc. are then collected, transferred to a platinum dish, and evaporated to constant weight on a water bath. By evaporating in the same manner 50 cc. of the infusion before treatment with hide powder, the difference in weight of the residues will give the amount of tannin in 50 cc. of the infusion.

It cannot be said that this gives the exact amount of tannin, but it does accurately determine the value of a sample for tanning purposes, since it represents just the substance which is absorbed by the hide.

The results are usually higher than those obtained by the permanganate method, and always considerably higher than those by precipitation with gelatin and alum.

Tannin extracts may be estimated by the same apparatus. Five to ten grammes of the extract are dissolved in a litre of water, and the filtered liquid used like the infusion of oak bark.

There are several other considerations in the valuation of an extract, and this will be taken up in a later volume, when the whole subject of extracts will be fully treated of.

The varying results reported by different investigators point to the necessity and importance of a uniform method of estimation. They also emphasize the demand for a more complete and thorough knowledge of the compounds we are endeavoring to estimate; for of

what use is the exactness claimed for the permanganate process if we do not know the value of the oak tannin in cubic centimetres of the permanganate solution? Until the study can be prosecuted further, we can do no better than adhere to the practical but rather unscientific hide powder method.

SECTION VI.

MANGROVE TANNIN.

History.

PROBABLY the first reference to mangrove tannin was made by Dr. James Howison in 1804, when he received a gold medal from the Society of Arts for his description and a sample of the extract made in India from four hundred pounds of the bark. The method of preparing this extract, however, was not such as to give the largest yield or the most satisfactory product. The extraction was carried on without the aid of heat, and the resulting liquor was evaporated by exposure to the sun until quite concentrated, when it was finished by the application of heat. There must have been considerable deterioration of the product by fermentation, as well as by the decomposition due to the application of direct heat.

This sample of fifty-four pounds cost eight shillings in Bengal, and the author thought it could be prepared for ten shillings per hundred-weight.

More recently, in 1846, we find a description of mangrove by W. Hamilton, in which he gives an interesting account of its manner of growth and possible uses in medicine and the arts.

Source.

Mangrove tannin is derived from the bark of the red mangrove, *Rhizophora mangle*. This tree is found

on the eastern side of tropical America. The young plants adhere to the rocks or shells of a reef, and soon a layer of mud is formed, which serves to support and nourish the additional shoots until an impenetrable thicket is formed. In many places the mangrove is nothing more than a shrub, but on the shores of Southern Florida it attains a height of thirty feet, and forms dense forests, whose descending root branches remind one most forcibly of the famous banyan-trees of India. After a time the mangrove forms a soil too high for itself to flourish on, and it is replaced by cedars and other trees. By this means the shores where it grows are constantly encroaching on the ocean.

The bark has been found to contain 23.92 per cent. tannin. The other constituents are those common to most plants, including 1.72 per cent. of mucilage, 0.81 per cent. of glucose, 7.02 per cent. of albuminoids, 4.27 per cent. of starch, and 27.49 per cent. of cellulose. There were also found 6.10 per cent. of ash in which sodium salts predominated, as might be expected from the situation in which the tree grows. The moisture in the air-dry bark amounts to 12.04 per cent., which would make the tannin in the absolutely dry bark 27.19 per cent.

Preparation and Purification.

The best menstruum with which to extract the tannin from mangrove bark is ether, having a specific gravity of 0.750. By this means the extraction of the large amount of anhydrides, or "reds," is avoided.

The ether is recovered from the extract by careful distillation until the latter is reduced to a small bulk,

and the concentration is continued under reduced pressure to dryness. The residue is obtained in a porous condition so as to be readily acted on by water. The solution in this latter solvent is filtered clear, and the filtrate divided in two parts; one half is completely precipitated by lead acetate and the other half stirred in. After standing a short time the mixture is filtered, and the filtrate agitated with acetic ether in successive portions until the tannin is removed. The acetic ether solution is distilled to dryness under reduced pressure, the residue dissolved in alcohol and ether, filtered, and the filtrate distilled to dryness in a vacuum, which yields the tannin in a porous, nearly white condition.

Properties and Composition.

The color of mangrove tannin, after repeated purification, is nearly white, but as usually prepared it varies from a dark brown to a light reddish-brown. Its solubility appears to be the same as that of most other tannins,—namely, complete solubility in water, alcohol, and commercial ether, but insolubility in absolute ether.

The following color reactions and precipitates indicate its behavior towards the usual tannin reagents :

Ferric chloride	Dirty-green ppt.
Ferric acetate	Olive-green color and ppt.
Calcium hydrate	Pink ppt., red on surface.
Bromine water	Yellow ppt.
Cobalt acetate	Faint cloudiness.
Uranium acetate	Red-brown color and ppt.
Potassium bichromate	Brown ppt.

The above reagents were applied to a 1 per cent. solution. No sugar was found associated with this tannin.

On the application of heat to this tannin in glycerin until the temperature reaches 215° , shaking out the decomposition products with ether, evaporating the latter, dissolving the residue in water, and applying the usual reagents, a catechol tannin is indicated.

When mangrove tannin is purified until it is of a light reddish-yellow color, and dried at 120° , it has been found to yield the following results on elementary analysis :

Carbon	59.76 per cent.
Hydrogen	4.69 “
Oxygen	35.55 “
	100.00 “

These results are an average of three combustions.

This corresponds closely to the percentage composition of rhatany tannin as determined by Raabe, to that found for horse-chestnut tannin by Rochleder, and to that for tormentilla tannin as determined by Rembold. There is also very little doubt but that it is identical with the tannins of canaigre and mimosa.

SECTION VII.

CANAIGRE TANNIN.

History.

CANAIGRE roots have been used by the Mexicans in tanning for over two centuries. On July 9, 1868, a package of these roots was forwarded for John James, of San Antonio, Texas, to the Agricultural Department at Washington, with a letter stating that F. Kälteyer, a chemist in that city, had found them to contain 32 per cent. of tannin. This sample was mislaid or overlooked until 1878, when it was reported on by the chemist.¹

It was then found to contain 23.45 per cent. of tannin. A fresh sample was also procured, and the tannin estimated in the fresh roots with identical results, after making due allowance for difference in moisture.

A report on canaigre by William Saunders was published in the Agricultural Report of 1879. He made clear its botanical origin, and his conclusions were accompanied by a lithographic plate of the plant in bloom.

Previous to the government publications, we find one in 1876 by Rudolph Voelcker on an analysis of the roots gathered in July, 1874. He found 23.16 per cent. of tannin, and proved the presence of

¹ Report of the Commissioner of Agriculture, 1878, p. 119.

chrysophanic acid and aporetin. He was not aware of the botanical origin of the plant, but supposed it belonged to the natural order *Polygonaceæ*.

There was an exhibit of these roots at the New Orleans Exposition in 1885-86, over which was the inscription "A New Tanning Material."

Following this, experiments were instituted in Chicago to determine the practical value of canaigre for tanning. Since then several attempts have been made to manufacture an extract on a commercial scale that would supplant the ground roots, and thus save the expenses of transportation. These experiments were partly successful in 1889, and have, more recently, by the establishment of factories in the immediate vicinity of the growing plant, become an assured success. The use of canaigre in tanning has passed the experimental stage, and has become an established industry. Considerable quantities are now shipped to Europe from Arizona, Texas, and New Mexico.

There appears to have been very little investigation made of the pure tannin of canaigre. Probably all that has been done previous to this date on its properties and composition was published by J. C. Peacock and myself in the *American Journal of Pharmacy* in 1893. This will be referred to in its appropriate place.

Source.

Canaigre tannin is obtained from the tuberous roots of the *Rumex hymenosepalus*, Torr.

The plant furnishing this root is found in the hot, dry localities of Southwestern United States and in Mexico. It is especially abundant in Texas, New

Mexico, and Arizona, and in a lesser degree in California, Utah, and Indian Territory.

It flourishes in a sandy soil so dry that other vegetation survives with difficulty. Although it grows so well in dry soil on the plains, it, nevertheless, thrives best and most luxuriantly in low sandy and gravelly soils near the rivers.

The valleys of the Salt and Gila Rivers of Arizona produce the plant in great abundance, and in the valleys of the Santa Cruz, San Pedro, and Rillito Rivers are large tracts, in which it is the prominent feature of the vegetation. According to Dr. Harvard it is found along the sand-hills near the Rio Grande in Texas, thirty feet or more above the level of the river. It is very susceptible to cultivation, and when stimulated by richer soil and irrigation, the results are very marked for the better.

The canaigre plant is from one to three feet in height, and in some respect resembles the common dock (*Rumex crispus*, L.). Fig. 31 represents the whole plant in bloom, and Fig. 32 a single tuber, the latter one-half natural size.

For the following detailed description of this plant the author is largely indebted to private communications from Professor C. B. Collingwood, of the University of Arizona, and to Bulletin No. 7, February, 1893, of the Agricultural Experiment Station, associated with the above university at Tucson. Professor Collingwood was one of the authors of the Bulletin.

A short description of the plant was published by Dr. V. Harvard, U.S.A., in the *Proceedings of the United States National Museum*, September 30, 1885.

FIG. 31.



Rumex hymenosepalus, Torr.
CANAIGRE.

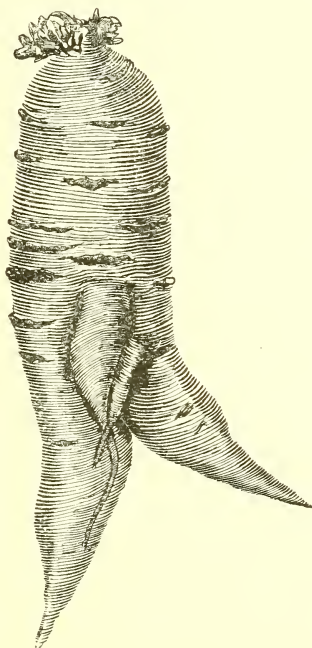
Further, Professor William Trelease described the plant in his paper, "A Revision of the North American Species of *Rumex* occurring North of Mexico," published in the Third Annual Report of the Missouri Botanical Garden, 1892.

The plant appears above ground about the 1st of February, after the winter rains, and by the last of April it is in full bloom.

After maturing seed, the top dies about the 1st of June, when the hot season commences. When the winter rains begin early, the plant will often appear above ground in November or December, in which case it grows slowly during the winter, since the climate of that locality is not sufficiently severe to destroy its foliage.

The seeds appear in great abundance, but very few are matured; propagation is effected, therefore, almost exclusively by the roots. These roots are found about a foot under the surface, in clusters of three or four, which sometimes lead to other clusters, so that a single plant often yields from ten to fifteen tubers. Each of these is from two to six inches

FIG. 32.



long and from one to two inches thick. Some are long and slender, others are nearly as broad as long. In weight they vary from a few ounces to over a pound. The exterior of the root is from a reddish-brown to a nearly black color, depending upon its age, and upon the amount of iron in the soil. Late in the summer a number of buds appear on the crown end of the tubers, ready for growth after the winter rains. The individual tubers appear to reach their full size at the close of the first season, but they continue to live, producing new roots and new plants each season, for several years.

“The roots of a year’s growth are a little more firm in texture than a potato; but when they finally die they become dry, hard, and nearly black throughout. In this condition they are as hard to cut as a piece of wood; and there is a large increase in the amount of coloring matter. By boiling, the root becomes softer, but does not break open and fall to pieces as the potato. The young roots are nearly white in the interior. As they grow older they become dark yellowish red, from the development of coloring matter within the cells.”

The following description of the structural characteristics of the root is taken from the Bulletin of the Arizona Experiment Station referred to above:

“The tissue of the root is mostly of large celled parenchyma, with a few wood cells and ducts scattered about here and there, but mostly toward the centre of the root. This tissue develops from a thick layer of cambium located in the nearly mature root at about a quarter of the distance from the epidermis to the centre. A rapid development of permanent parenchyma tissue takes place at either side of the cambium zone; how-

ever, as we would expect, the wood cells and ducts are all within the cambium ring. The parenchyma without is much the same as that within, only the cells are shorter and much wider. The root has a very regular structure, but is quite remarkable in the large development of tissue outside the cambium zone. This tissue will frequently nearly equal in weight that within, and is as easily separated from it as the bark is peeled from a tree. The bark is rather brittle, but will break cross-wise much more easily than longitudinally."

The important constituents of canaigre are tannin and starch. There are, however, results of two or more analyses on record which include a determination and estimation of the other principles. The first appears to have been made in 1876 by R u d o l p h F. G. V o e l c k e r. His material came under the name of "Raiz del Indico," and, except that it belonged to the natural order *Polygonaceæ*, nothing was known of its botanical origin. The description of the plant's habits and of the roots corresponds exactly with that of canaigre.

The constituents as determined by V o e l c k e r were, chrysophanic acid, tannin which gave a black with ferric chloride, "but did not yield pyrogallie acid," aporetin phæoretin, and erythroretin, together with some of the usual constituents of plants. The leaves were found to contain malic and oxalic acids in combination with calcium. The author evidently worked with the expectation of finding a similarity in the constituents to those of rhubarb.

The government analysis in 1878 apparently had the same object in view, of showing a relation to rhubarb, as may be seen by the following summary :

Emodin ?	Trace	} Soluble in alcohol.
Yellow resin	0.93	
Red substance, soluble in alcohol	10.48	
Red substance, soluble in water	10.44	} Soluble in water.
Sugar	10 00	
Rheo-tannic acid	23.45	
Gum, pectin, brown color	6.41	
Albuminoids	5.21	
Aporetin	4.78	
Starch	8.00	
Cellulose	4.52	
Ash	4.38	
Moisture	11.17	
	99.77	

In the above analysis the air-dry roots were used, but examinations were likewise made of the green roots, in which were found 68.07 per cent. of moisture and 8.51 per cent. of tannin, corresponding to 26.62 per cent. of tannin in the water free substance. "The air-dry roots contained 11.17 per cent. moisture, equivalent to 23.30 per cent. tannin in the strictly dry root."

The conclusions drawn were as follows :

"From the close agreement in the tannin estimations it would seem as if the tannin was not affected by long keeping.

"This tannic acid is of the variety known as rheo-tannic acid, and is identical with that existing in rhubarb. In many respects canaigre resembles rhubarb."

Other investigators have given somewhat different figures for the percentage of tannin in the root. Professor Collingwood found a variation in fourteen samples from different localities and soils of Arizona of from 22.5 per cent. to 35.6 per cent., and an average of 30.52 per cent. "Of many other samples

obtained both from this Territory (Arizona) and New Mexico the average content of tannic acid is about the same."

The following results by the same authority show the percentage of tannin in the air-dry roots at different seasons of the year :

June 4, 1892	16.7 per cent.
August 2, 1892	18.2 "
September 13, 1892	23.1 "
October 15, 1892	23.0 "
November 16, 1892	24.4 "
January 10, 1893	25.0 "
January 17, 1893	28.2 "

The young roots when first formed contain about 3.9 per cent. tannin in the green state, or 15 to 16 per cent. when dry.

"At this time the roots are white with a yellowish ring, and do not turn red even on exposure to air.

"After blossoming the roots appear to have attained their full size, are somewhat deeper in color, and contain but little more tannic acid than when younger.

"Through the long hot summer they gradually increase in tannic acid.

"As soon as they sprout and grow there is a marked tendency to increase in tannic acid.

"Analyses of roots of the same age, sprouted and not sprouted, show the sprouted roots to have been uniformly higher in tannic acid.

"It may be found that two qualities of roots will be obtained : the first, one-year roots, with about 23 to 25 per cent. of tannic acid and only a small amount of coloring matter ; the second, two-year roots, with

higher percentage of tannic acid and larger amount of coloring matter."

My own experience in roots of different ages, furnished to me by Mr. Allaire, of Deming, New Mexico, has shown the percentage of tannin in those of two years' growth to be the highest, amounting in the air-dry roots to 30.60 per cent. Older roots yielded nearly as much tannin, but the amount of coloring was so great as to be a positive disadvantage. The best known methods of estimating tannin give a certain proportion of this coloring as tannin.

Experiments are in progress in Arizona that will demonstrate the possibilities of cultivating canaigre. The wild roots, although very abundant at the present time, would not long supply the demand if their use to replace gambir should become general. Thus far the experiments have indicated that cultivation may be conducted successfully, and at the same time demonstrated that the percentage of tannin does not decrease under cultivation, but, on the contrary, tends to increase. An important and interesting constituent of the root is starch, which, according to the government analysis, amounts to 18 per cent. This is probably the only tanning material containing such a large percentage of starch.

Professor Collingwood reports on the starch and coloring matter as follows:

"All the parenchyma tissue is well filled with starch. Even the roots a few weeks old are not lacking in this respect. The granules are large and assume many different forms; however, as a rule they are oblong to ovate.

“The nucleus or centre of growth is fairly well defined and a little to one end. The large granules all show concentric layers.

“Cells here and there are filled, or partly filled, with a yellowish-red material, which gives the root its characteristic color.

“In some of the cells we see glistening pieces of a yellow resin. Only a part of the coloring matter is dissolved out by the action of water. If a root be freshly cut, a gum-like substance, containing starch granules and more or less coloring matter, will exude from the cut surface. In a few days this becomes quite hard and of a brownish color. The cells towards the centre of the root contain the largest amount of coloring matter.

“Frequently it is most abundant in three to five concentric layers extending from the centre towards the outside, these layers alternating with lighter ones. Sometimes it seems to be evenly distributed throughout the entire root. The amount of coloring matter increases with the age of the root, as may be readily observed by comparing roots of different age.

“In addition to these varied coloring materials, many parenchyma cells contain large compound crystals, probably of calcic oxalate. These crystals were all observed in the tissue outside the cambium. Similar crystals, likely of the same material, were found in large numbers.”

PREPARATION.

Two methods for the preparation of the pure tannin of canaigre have been tried by the author, one, by extracting the root with commercial ether (specific gravity

0.750), and the other by percolating with cold water. The product from the ether extraction was found to be very difficult to purify from the accompanying coloring matter. The same objection would apply to the use of acetone, which, since the above experiments, has been found so valuable for the extraction of the oak tannins. Cold water, therefore, may be considered the most desirable solvent. Hot water is excluded on account of the large percentage of starch present.

The cold-water percolate is first freed from coloring matter as far as possible by fractional precipitation with lead acetate. This is best accomplished by dividing the percolate in two parts, completely precipitating one portion by the lead salt, then stirring in the other portion and filtering. The resulting filtrate is of a clear yellow color. The tannin is removed from the filtrate by agitation with acetic ether. The latter solvent is removed by distillation under reduced pressure, the residue dissolved in commercial ether, filtered, and the filtrate distilled to dryness in a vacuum. By this means the tannin is obtained in a porous condition, and is free from odor of acetic ether. The residue is then digested with absolute ether, which removes coloring matter and crystalline substance. The latter has been found to consist of protocathechuic acid.

Other methods for the preparation of this tannin have been tried by the author; one of these consisted in completely precipitating it from aqueous solution by lead acetate, and decomposing the lead salt by hydrogen sulphide. In this case the lead sulphide is found to be a good decolorizing agent, but the loss of tannin is excessive. Another method which has been tried in-

volves the precipitation of the tannin by sodium chloride. The tannin in this case, however, is mixed with a reddish-brown coloring matter, probably an anhydride, and is difficult to further purify. By agitating the filtrate, after precipitation by salt, with acetic ether, a very small quantity of a light-colored tannin is obtained, similar in properties to that of the cold water process.

PROPERTIES AND COMPOSITION.

Canaigre tannin is of a yellowish-white color. It is readily and completely soluble in water, alcohol, and glycerin. Ether containing alcohol and water dissolves it, but absolute ether has little solvent action on it.

A 1 per cent. solution of this tannin gives the following reactions :

Ferric chloride	Green ppt.
Ferrous sulphate	No change.
Lead acetate	Yellowish ppt.
Gelatin and alum	Yellow ppt.
Potassium bichromate	Greenish-brown ppt., darkening.
Calcium hydrate	Light pink ppt. turning red, then brown.
Bromine water	First yellow, then brown ppt.
Cobalt acetate	Yellow ppt.
Uranium acetate	Crimson color, becoming a red- brown ppt.
Ferric acetate	Green ppt.

The reactions are practically those of all tannins which give green precipitates with salts of iron.

The precipitate by bromine water has been found, on separation and washing, to contain bromine.

On subjecting the tannin to a temperature of from 160° to 190° catechol is formed.

When the tannin is boiled for three hours with a 2 per cent. solution of absolute hydrochloric acid, an amorphous, red, insoluble substance separates. Protocatechuic acid is formed at the same time, as may be shown by filtering off the red coloring, and agitating the filtrate with ether. On separating the latter and evaporating spontaneously, the protocatechuic acid is deposited.

Sugar is not formed in the decomposition by acids.

When the tannin is fused with potassium hydrate, the mass dissolves in water clear, and on neutralizing the alkali with diluted sulphuric acid, and agitating the unfiltered mixture with ether, the latter deposits protocatechuic acid on evaporation. Phloroglucol does not appear to be formed.

An acetyl derivative appears to be formed when the tannin is boiled with acetic anhydride for an hour. The resulting solution when poured into water separates a white plastic mass, which has a melting point between 100° and 120° . A further investigation of this substance is desirable.

The composition has been determined by elementary analysis, with the following results :

Carbon	58.10 per cent.
Hydrogen	5.33 "
Oxygen	36.57 "
	100.00 "

These figures represent the average of three analyses. The substance had previously been dried at 120° .

The percentages indicate that canaigre tannin closely agrees in composition with the tannins from mangrove, rhatany, and, perhaps, mimosa.

SECTION VIII.

CHESTNUT TANNIN.

History.

MOST of the references to chestnut tannin in the literature of the subject really belong to the product from the horse-chestnut, *Æsculus Hippocastanum*, L., which was studied by Rochleder over forty years ago. Since that time it has attracted very little attention, and is of little, if any, practical value.

The true chestnut tannin, from *Castanea vesca*, Gaertner, or *Castanea dentata*, Marshall, has been but very little studied, apparently not at all previous to 1884. It is of great commercial value, an extract of the wood and bark being extensively manufactured, and employed in both this country and France for tanning and dyeing.

The value of the wood, because of its tannin, first attracted attention in the early part of this century, and in 1819, William Sheldon communicated to the *American Journal of Science* his discoveries and views on the "Application of Chestnut Wood to the Arts of Tanning and Dyeing." The editor (Silliman) prefaced the communication with some favorable remarks, to the effect that having repeated some of the experiments he was well satisfied that the discoverer had not overrated or erroneously estimated the value of his own results. He says "that the highly *useful* arts alluded to will derive important aid from the use of a material so abundant and cheap as chestnut wood."

Sheldon maintained "that the chestnut *wood* contains twice as much tannin as *ross'd oak bark*," and that he had uniform success with it in a great variety of experiments in tanning and dyeing. "The leather tanned with it has, in every instance, been superior to that tanned in a comparative experiment with oak bark; being firmer, less porous, and at the same time more pliable." He further found, "As might be expected, the inspissated aqueous extract of chestnut bears a close resemblance in many respects to catechu."

From that time we find little reference to chestnut tannin until a very recent period, although the extract gradually came to be an article of commerce. The results of the first intelligent investigation of this tannin were published in 1884, by Paul Nass, in an inaugural dissertation at Dorpat, Russia. The chief regret concerning this work is that he used as the source of his supply the commercial extract of chestnut wood. Many investigations have been made based on commercial products, but this one is often adulterated with cheaper materials, and from carelessness in manufacturing still oftener contains the extract from woods other than chestnut. Unlike the admixtures in many other products, these are difficult, if not impossible, to detect.

If we assume that a pure extract was used, then in the course of its preparation the tannin contained therein might easily have undergone some change or decomposition. The further discussion of this contribution will be reserved until the composition of the tannin is considered. In 1891 the author of this volume published a contribution on Chestnut Wood Tannin, and in

1892 this was followed by one on the Tannin of Chestnut Bark. These will likewise be discussed later.

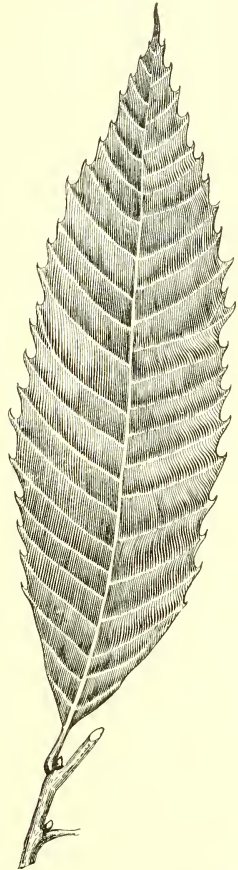
Considering the technical value of this tanning agent, the literature of the subject is very meagre, and it is believed that the above references cover nearly all that has been published on the constituents of chestnut.

Sources.

The sources of chestnut tannin are the bark and wood of the *Castanea vesca*, Gaertner. It is a tree sixty to eighty feet in height, and is found from Southern Maine to Delaware, and westward to Indiana and Michigan. Along the Alleghany Mountains it extends as far south as Alabama. It attains its finest growth on the western slope of the southern Alleghany Mountains.

The tree is readily distinguished by its narrow leaves, as shown in Fig. 33. When young it resembles the Chestnut Oak, but the bark remains smooth longer than that of the latter. The inflorescence and fruit are char-

FIG. 33.



Castanea vesca, Gaertner.
CHESTNUT.

acteristics by which it is distinguished from all other trees.

The fruit of the American variety is somewhat smaller and of finer flavor than that of European growth. Many of the European varieties are cultivated in this country under the name of Spanish chestnut. The fruit is a valuable article of food, and the wood is used in a great number of ways, in building, cabinet work, and for fencing.

The most valuable constituent of the chestnut wood is its tannin. This has been found by the author to be 7.85 per cent. of the air-dry chips. From the bark of a tree cut in August there were found 7.31 per cent. of the same tannin. Sheldon, more than seventy years ago, under the same conditions found 6.66 to 7.76 per cent. tannin in the wood.

The following is a summary of the constituents found in the wood :

Crystalline wax, melting at 50°, soluble in hot 95 per cent. and in absolute alcohol	1.03 per cent.
Gallic acid	.05 "
Resin extracted by ether	.28 "
Tannin extracted by absolute alcohol	3.42 "
Mucilage	1.15 "
Dextrin	1.89 "
Glucose	.96 "
Tannin extracted by water	1.92 "
Pectin and Albuminoids	1.46 "
Extractive dissolved by dilute acid	2.95 "
Ash	0.67 "
Moisture	7.05 "
Lignose and Cellulose	70.76 "
Undetermined and Loss	6.41 "
	100.00 "

It is probable that gallic acid does not pre-exist in the wood, but was formed during the above analysis as the result of decomposition. The constituents of the bark were not found to differ materially, except in relative proportion, from those in the wood. The ash of the bark was found to be 4.71 per cent.

Preparation.

In the preparation of this tannin Nass used the commercial extract, which had been made on a large scale by boiling the chipped wood with water.

My own experience has been by extracting the finely-powdered wood or bark with commercial ether (specific gravity 0.750). There is no reason why acetone should not be used as it has been in the preparation of the oak tannins. After the tannin has been extracted and the solvent recovered, the next step is to treat the residual extract with water containing a small quantity of alcohol, say 10 per cent. By this process the resin and some red coloring matter are left undissolved, and the tannin goes into solution. This solution is then agitated with ether to remove gallic acid, and then the tannin is removed by agitation with successive portions of acetic ether. The acetic ether is recovered, the residue dissolved in water, and the resulting solution agitated with acetic ether until the tannin is removed; this process of solution in water and shaking out with acetic ether is repeated until the tannin becomes readily and completely soluble in water, and is nearly white in color. The tannin is then dissolved in commercial ether (specific gravity 0.750), and the solution filtered, if necessary, then distilled, first under ordinary pressure,

and finally in a vacuum until dry. By this means all odor of acetic ether is removed. The dry residue is then digested with absolute ether, by which gallic acid and minute quantities of resinous products are removed, and after pouring off the ether the residue is dried in a vacuum on a water bath. The product should be nearly white, porous, and readily and completely soluble in water.

On precipitating an aqueous solution of it by lead acetate, removing the excess of lead salt from the filtrate by hydrogen sulphide, and the latter by gentle warming, the filtrate should not reduce Fehling's test, showing the absence of sugar.

Properties.

Chestnut tannin, whether prepared from the wood or the bark, is almost white in color, and soluble in water, alcohol, ether, and glycerin.

A 1 per cent. solution of the tannin gives the following reactions, compared with the same reactions of gallotannic acid :

Reagent.	Chestnut Tannin.	Gallotannic Acid.
Ferrous salt.	No change.	No change.
Ammonio-ferric alum.	Blue-black ppt.	Blue-black ppt.
Tartar emetic and Ammonium chloride.	} Slight clouding. } Pale ppt.	Slight clouding. Pale ppt.
Bromine water.	No ppt.	No ppt.
Calcium hydrate.	Light ppt. turning light blue.	White ppt. turning light blue.
Sulphuric acid (1 to 9).	No deposit on boiling.	No deposit on boiling.

On slowly heating chestnut tannin to 200° it is converted into pyro- and metagallic acids. An acetyl compound of this tannin has been prepared by dissolving it in acetic anhydride. This acetyl derivative closely resembles that obtained from gallotannic acid.

Composition.

Nass used three methods of preparing the chestnut tannin. In all of these the commercial extract was employed as the source.

First he fractionally precipitated the aqueous solution of the extract by common salt. Rejecting the first portions, which consisted of phlobaphene, each of the other three fractions was purified by dialysis, and the tannin then removed by agitation with acetic ether.

The second method consisted in taking the filtered liquid from which the tannin had been precipitated by common salt and agitating it with acetic ether. By evaporation of this acetic ether a tannin was obtained differing in composition from that prepared by the preceding method. Nass called the former of these the dialysis process, and the second the process by agitation with acetic ether.

A third method was tried in which an aqueous solution of the extract was fractionally precipitated by lead acetate. The first fraction was rejected, and the next collected on a filter and carefully washed with recently boiled distilled water. The precipitate was suspended in water and decomposed with hydrogen sulphide. The filtrate from the lead sulphide was subjected to a stream of carbon dioxide and then gently warmed, by which the hydrogen sulphide was removed. The solution

was then concentrated in a vacuum to a syrupy consistence, and finally dried over sulphuric acid.

The following comparison of the combustion results shows on what foundation Nass based his statement that there existed two distinct tannins in chestnut wood.

The figures for the dialyzed tannin are the average of five analyses, those of the lead acetate product of two, and those of the product obtained by agitation with acetic ether of five analyses. The substance was previously dried at 110° .

	Dialyzed Tannin.	Lead Acetate Tannin.	Acetic Ether Tannin.
Carbon	52.20	51.80	53.63
Hydrogen	3.97	3.69	4.59

Nass concluded that the first two were identical. Each contained some ash. He assigned for this tannin the formula $C_{17}H_{14}O_{11}$. To the other he gave the formula $C_{17}H_{18}O_9$. He evidently had in mind Etti's oak tannin, $C_{17}H_{16}O_9$, for he calls attention to the fact that the tannin he obtained by agitation with acetic ether differed from Etti's by one molecule of water only. He thought the one having the formula $C_{17}H_{14}O_{11}$ might possibly be an oxidation product of the other. He evidently did not seriously consider that it might be identical with gallotannic acid, although he noted the fact that it had nearly the same percentage composition. The fact that he found considerable quantities of gallic acid should have convinced him that he had a compound not very closely related to the oak tannins.

My own analyses of the tannins prepared directly

from the wood and bark of the chestnut gave the following results :

	Chestnut Wood Tannin.	Chestnut Bark Tannin.	Gallotannic Acid.
Carbon	52.42	52.11	52.17
Hydrogen	4.67	4.40	3.10

It may be thought that the figures for hydrogen in the above analyses are too high to admit of the chestnut tannin being identical with that from nutgalls, but it is well known that in the combustion of gallotannic acid the hydrogen is always high unless the product has been dried at from 130° to 140° . These tannins were heated to 120° before combustion. It seems probable, therefore, that the tannins from chestnut wood and bark are identical with that from nutgalls. It is, however, difficult to prepare it in as pure a condition. There is a red coloring matter associated with chestnut tannin which in many of its properties resembles the anhydrides found in oak bark. The chestnut wood contains a small proportion only, but in the bark it occurs rather more abundantly. There is still a large field in which to investigate this tannin. The decomposition products as determined by Nass should be still further studied and his results confirmed or refuted.

Estimation.

The estimation of chestnut tannin may be accomplished in the same manner as that of the oak. Both wood and bark are easily extracted by water, since they are quite porous. The process with gelatin and alum as detailed in Volume I., page 38, of this work, has always been satisfactory in the author's hands for these

substances. In chestnut there is not the accompanying coloring matter to interfere that there is in the oak. The hide powder process as given under the oak tannins, in this volume, has been tried with satisfactory results.

Applications.

This tannin is used almost exclusively in the form of extract. It appears in commerce in both liquid and solid form. The liquid extract is either 42° or 51° Twaddle, contains 45 to 55 per cent. of solid matter, and 15 to 20 per cent. tannin. The solid extract, from 80 to 90 per cent. solid matter, and 20 to 30 per cent. tannin. The French extract is usually drier than the American. Both are often adulterated with molasses or glucose. When the former is used the increase of ash is an indication of its presence. The ash of pure solid extract of chestnut should not exceed 2 per cent. and is often less; the liquid extracts should yield proportionately less. This test also serves to indicate an admixture of oak extracts, which always contain more ash.

The extract is made most extensively in Pennsylvania and Virginia. The works are usually situated in the mountain districts, where the supply of the wood in the immediate vicinity is sufficient to obviate the necessity of much transportation. In this country the logs are cut into lengths of from four to five feet, the larger ones are split, and then they are chipped by heavy machinery especially constructed for the purpose, the cutting being directly across the grain of the wood. In France the wood is cut into smaller pieces, and the chipping much oftener takes the form of rasp-

ing, by which the wood is obtained in a condition to be readily extracted by water.

The extraction of the chips is carried out in wooden or copper boilers ; in a few cases iron has been employed with satisfactory results. The objection sometimes advanced that iron blackens the product does not apply when large quantities are continually in process of extraction. When wooden vessels are employed, the extraction is conducted at the temperature of boiling water. With closed copper or iron extractors, the temperature is often raised above 100°. When this excess is not more than five or ten degrees, the wood is more rapidly and thoroughly exhausted, and the product is not injured as much as it would be by the long boiling necessary for exhaustion in open vessels. It is, however, a nice point to decide when the advantages of rapid extraction end, and when the disadvantages of too high a temperature begin.

Water is, or should be, the menstruum for such an easily decomposable substance. Suggestions have been made and patents have been granted for the employment of sulphuric acid and various other substances as additions to the menstruum. Such additions cannot be of any value to an extract that depends for its value on the undecomposed tannin present.

The evaporation is best accomplished in vacuum-pans, although this is not always done. When too high a temperature is used in extracting, or where the evaporation is conducted without the use of vacuum, the product contains much insoluble and resin-like matter, which interferes with its application in both of the industries in which it is employed. It is impossi-

ble to prepare a good solid extract without the use of a vacuum-pan for the evaporation.

A good extract of chestnut is especially valuable in dyeing when it is desired to produce a "dead" black. In tanning it is much used to correct the color of less expensive tanning materials.

SECTION IX.

CONCLUSIONS.

THE author has been repeatedly appealed to for some classification of the tannins. It has been stated in the Introduction that no *final* classification could be attempted at this stage of the work, and the suggestion was there ventured that the tannins would eventually be grouped according to their composition and chemical properties.

In looking over the composition of those discussed in this volume, and comparing them with what appear to be trustworthy results obtained in recent years by other investigators, we find they all arrange themselves, according to their percentage of carbon and hydrogen, into the following two groups :

	I. The Gall Tannin Group.	II. The Oak Tannin Group.
Carbon	52.17	60.00
Hydrogen	3.10	5.00

The above percentages in the first of these groups are calculated from the generally accepted formula of digallic anhydride ; in the second group the even numbers are taken because of their very close agreement with the general average found, not only of the oak tannins, but also of those classified with them.

If now we make a list of those tannins whose com-

position has been given in this volume, and include some additional ones recently studied by others, we get the two groups as follows :

<i>Group I.</i>		
	Carbon.	Hydrogen.
Gallotannic Acid	52.10	3.52
Chestnut Wood Tannin	52.11	4.40
Chestnut Bark Tannin	52.42	4.67
Pomegranate Bark Tannin (Culley)	50.49	3.99
Chestnut Tannin (Nass)	52.07	3.97
Sumac Tannin (Löwe)	52.42	3.56

<i>Group II.</i>		
	Carbon.	Hydrogen.
Oak Bark Tannin, average of nine species . .	59.79	5.08
Mangrove Tannin	59.76	4.69
Canaigre Tannin	58.10	5.33
Rhatany Tannin (Ohmeyer)	59.20	4.72
Oak Bark Tannin (Etti)	59.29	4.99
White Oak Bark Tannin (Kraemer)	59.65	4.65
Kino Tannin (Bergholz)	59.65	4.87
Catechu Tannin (Löwe)	61.93	4.80
Tormentil Tannin (Rembold)	60.75	4.65

The fact of similar percentage composition would not in itself be sufficient to group the above tannins, as there are many other organic compounds that do not vary widely in their composition from these.

When, however, we take certain reagents, we find the classification into the above groups still holds, as follows :

	Group I.	Group II.
Ferrie salts	Blue color and ppt.	Green color and ppt.
Calcium hydrate	White ppt., becoming blue.	Light pink ppt., becoming red and brown.
· Bromine water	No ppt.	Yellow ppt., becoming brown.

There are many other reactions common to both groups, but the above reagents distinguish sharply between the two.

Then the decompositions of the above tannins by heat, by acids, and by alkalies again further confirm the above grouping.

With the above facts in view the conclusion naturally forces itself upon us that there are two groups of the tannins; there are, however, the results of many investigators to account for and reconcile.

It is claimed for some tannins that they are insoluble in water, for others that they are not precipitated by gelatin, and so on through all the possible exceptions. Compounds, however, which are distinguished by such peculiar behavior do not belong with the tannins at all.

With so many properties in common we cannot expect there exist many groups. We naturally look for only one; the facts, however, demand at least two; a close chemical relation, therefore, probably exists between these two; to discover that relation and classify the remaining uninvestigated members still offers a most attractive field to the plant chemist.



AN INDEX
TO THE
LITERATURE OF THE TANNINS.

EXPLANATORY NOTE.

THE same method of stating titles and authors has been continued that was adopted in Volume I. One of the principal reasons for this is that the bibliography of a subject is often an important contribution to its history, and by copying the titles just as they appear in the original papers we add considerably to their value.

The order of arrangement is a chronological one, which is also of great assistance in studying the subject historically.

The constant factors in a reference, one or both of which is generally known, are the date and the author. By this chronological arrangement the former is easily found, and by the separate index of authors the latter is also readily turned to.

A few of the references given in Volume I. have been repeated in this index, but this has only been done where the titles in the former were not complete, or the original source not given. This has been notably the case with those papers from "*Sitzungsberichte der kaiserlichen Akademie der Wissenschaften zu Wien*," all of which are here inserted at a risk of repeating a few ; the author having, in the mean time, been able to consult a complete set of the above publication.

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THE END.

